PB-239 749

THE FATE OF SELECT PESTICIDES IN THE AQUATIC ENVIRONMENT

James R. Sanborn

Illinois University

Prepared for:

National Environmental Research Center
Illinois State Natural History Survey

December 1974

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SELECTED WATER RESOURCES ABSTRACTS

INPUT TRANSACTION FORM

1. Report No.

2.

PB 239 749

THE FATE OF SELECT PESTICIDES IN THE AQUATIC ENVIRONMENT

5. Report Date

6.

8. Performing Organization Report No.

Sanborn, James R.

Illinois Natural History Survey and
Board of Trustees, University of Illinois,
Urbana, Illinois

10. Project No. R-800736

11. Contract/Grant No. Grant R-800736

13. Type of Report and Period Covered Final

12. Sponsoring Organization ENVIRONMENTAL PROTECTION AGENCY

In this study 17 organic pesticides and five industrial chemicals were examined in a terrestrial-aquatic model ecosystem in an effort to determine their persistence and accumulation by the organisms of this system. Several classes of pesticides are represented as one or more insecticides, herbicides, miticides or plasticizers were investigated in this system. The use of this system for examining uptake and persistence of widely used agricultural chemicals provides the necessary data for comparison of field data to provide a framework which can be used to assess the potential environmental impact of new pesticides before they are given a recommendation for generalized use.

The data obtained from this work suggest that this model ecosystem is useful for the determination of the uptake and persistence of pesticides by the organisms. In general, it was found that most chemicals, with the exception of the persistent soil insecticide, dieldrin, underwent extensive degradation under the experimental conditions of the system. Dieldrin was exceptional in its behavior in that >96% of the radioactivity isolated from the organisms was unchanged dieldrin, clearly indicating the extreme inertness of this chlorinated hydrocarbon to undergo biological or chemical modification.

*Ecosystems, Trophic levels, *Pollutants, *Pesticide residues, *Biodegradation, Ecological distribution

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Model ecosystem, Insecticides, Herbicides, Plasticizers, Polychlorinated Biphenyls, Bux, Carbaryl, Carbofuran, Dieldrin, Lindane, Orthene, Parathion, Alachlor, Propachlor, Bladex, Bentazon, Dicamba, Pyrazon, 2,4-Dichlorophenoxyacetic Acid, Trifluralin, Banomite, DOP, Chlorinated Biphenyls, Captan, Hexachlorophene, Fish, Snail, Algae

ØSA, Ø5B

PRICE SUBJECT TO CHANGE

17. Security Class

Number of Pages 93

Price 3.00

Send To:

WATER RESOURCES SCIENTIFIC INFORMATION CENTER
U.S. DEPARTMENT OF THE INTERIOR
WASHINGTON, D. C. 20240

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☆ U.S. GOVERNMENT PRINTING OFFICE: 1975—697-819/77 REGION 10

EPA-660/3-74-025
December 1974

THE FATE OF SELECT PESTICIDES IN THE AQUATIC ENVIRONMENT

by

James R. Sanborn

Project R-800736
Program Element 1BA023
ROAP 21 AIM, Task 02

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Washington, D.C. 20402 SN-5501 00995

ABSTRACT

In this study 17 organic pesticides and five industrial chemicals were examined in a terrestrial-aquatic model ecosystem in an effort to determine their persistence and accumulation by the organisms of this system. Several classes of pesticides are represented as one or more insecticides, herbicides, miticides or plasticizers were investigated in this system. The use of this system for examining uptake and persistence of widely used agricultural chemicals provides the necessary data for comparison of field data to provide a framework which can be used to assess the potential environmental impact of new pesticides before they are given a recommendation for generalized use.

The data obtained from this work suggest that this model ecosystem is useful for the determination of the uptake and persistence of pesticides by the organisms. In general, it was found that most chemicals, with the exception of the persistent soil insecticide, dieldrin, underwent extensive degradation under the experimental conditions of the system. Dieldrin was exceptional in its behavior in that > 96% of the radioactivity isolated from the organisms was unchanged dieldrin, clearly indicating the extreme inertness of this chlorinated hydrocarbon to undergo biological or chemical modification.

This report was submitted in fulfillment of Project R-800736 by the Illinois Natural History Survey and Board of Trustees, University of Illinois, under the sponsorship of the Environmental Protection Agency. Work was completed as of June 30, 1973.

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ACKNOWLEDGEMENTS

The author would like to acknowledge several persons during this investigation. The initial studies were directed by Dr. G. M. Booth and carried out by Drs. Ching-Chieh Yu and Dale J. Hansen. Also, an acknowledgment is in order for Dr. William F. Childers and Mr. Lowell Davis who reared the aquatic organisms and provided useful information regarding the proper procedures for the maintenance of these organisms. Valuable discussions with Professor Robert L. Metcalf, the developer of this system, provided important insights regarding the interpretation of segments of the data in this report. In addition, the skillful assistance of M. Kathryn McClendon who helped finish the latter stages of this work as well as provided assistance during the preparation of this report is acknowledged. Finally, the outstanding laboratory facilities of the Illinois Natural History Survey and the University of Illinois are gratefully acknowledged.

SECTION I

CONCLUSION

The data presented in this report demonstrate the usefulness of a terrestrial-aquatic model ecosystem for the prediction of the persistence and uptake of selected organic chemicals. Only the soil insecticide, dieldrin, and the herbicide, Trifluralin®, were found to accumulate over the concentration in the water in the fish and snail. The experiment with lindane and the extender, Aroclor® 5460, yielded information that indicated the snail accumulation was unaffected as compared to lindane examined alone in this system, while the fish accumulation was increased slightly. Other chemicals examined in this system were three pure ^{14}C labeled polychlorinated biphenyls which accumulated in increasing amounts in the fish and snail as the number of chlorine substituents was increased. In addition, investigation of the fate of the phthalate plasticizer, di-n-octyl phthalate (DOP), demonstrated substantial accumulation in the fish and snail. Neither the bacteriostat, hexachlorophene, the fungicide, captan, nor the miticide, Banomite®, accumulated to significant amounts in the fish or snail.

SECTION II

INTRODUCTION

The utilization of a model ecosystem to examine the persistence and uptake of pesticides, or any other organic or inorganic chemical, has been shown recently to be a valid method for predicting the behavior of these materials in a terrestrial-aquatic environment (Metcalf et al., 1971; Metcalf et al., 1973). Though it has been adequately described before, a brief description of the terrestrial-aquatic model ecosystem will be useful for interpreting the contents of this report.

The system is housed in a glass aquaria (25 x 30 x 45 cm) and contains a sand-water interface consisting of 15 kg of sterilized white quartz sand and 7 liters of standard reference water (Freeman, 1953). Sorghum (Sorghum halpense) is grown in the sand to a height of 10-12 cm which is then treated on the leaves with 5 mg of a radiolabeled pesticide dissolved in acetone. Each compound was run in duplicate through the model ecosystem. The design of this system and treatment level correspond to a farm pond surrounded by a watershed under cultivation that has been treated 1 lb/acre (≈1.12 kg/hectare). After the sorghum has been treated, saltmarsh caterpillar larvae (Estigmene acrea) are added to eat the treated plant and therefore simulate both the first member of a food chain as well as act as an effective distributing agent for the labeled pesticide inside the system. The water contains several members of a fresh water aquatic food chain: namely, snails (Physa sp.), water fleas (Daphnia magna) and green filamentous algae (Oedogonium cardiacum).

After 27 days mosquito larvae are added to the system to become another member of the food chain and 3 days later a mosquito fish (Gambusia affinis) is added to become the final segment of the system. At the end of 33 days the entire system is taken apart and the organisms and water are analyzed for radioactivity by extraction with organic solvents and quantitation is carried out by counting the extracts by liquid scintillation techniques. In addition, the extracts are spotted on thin-layer chromatographic plates, developed with appropriate solvents and exposed to X-ray film to locate and identify the chemical composition of the solvent extracts. Identification of metabolites is made by co-chromatography with proposed metabolites as well as techniques of infrared, nuclear magnetic resonance and mass spectrometry. Once the identity of the metabolites or degradation products is known, then quantitative determination can be made on the propensity of an organic chemical or its metabolites to be concentrated from the water by the organisms of the system.

SECTION III

EXAMINATION OF SELECT INSECTICIDES

The first segment of this report is concerned with the behavior of select insecticides in the model ecosystem. Initially, the system was operated with several additional organisms besides the standard fish, snail, mosquito, Daphnia and algae; but later it was decided to delete these additional organisms so that more valid comparisons could be made with data derived by other investigators using the system developed by R. L. Metcalf and co-workers.

Bux®

The first insecticide examined is the carbamate insecticide, Bux®, which is a 3:1 mixture of m-(1-ethylpropyl)phenyl N-methylcarbamate and m-(1-methylbutyl)phenyl N-methylcarbamate. This insecticide has shown promise as a soil insecticide for control of pests under corn. It is moderately toxic to warm-blooded animals as it has acute oral and chronic LD_{50}'s of 87 and 400 mg/kg to the rat. The metabolism of m-(1-methylbutyl)phenyl N-methylcarbamate has been examined in rats and the primary excretion products found in the urine are conjugates of the phenol, m-(1-methylbutyl)phenyl N-hydroxymethyl methylcarbamate and m-(1-methyl-1-hydroxybutyl)phenyl N-methylcarbamate (Sutherland et al., 1970). Further, application of Bux® to the soil in which maize was grown resulted in no carbamate residues in the plants and primary metabolites isolated from the soil were the result of hydrolysis of the carbamate to the phenol and oxidation of Bux® to m-(1-methyl-1-hydroxybutyl)phenyl N-methylcarbamate. From these studies it was calculated that Bux® had a soil half-life between 1-3 weeks (Knaak, 1971).

Examination of the data in Tables 1 and 2 suggest that Bux® is a non-persistent insecticide as none of the snails, mosquitoes or fish contain residues of the intact insecticide. Further, the extractable radioactivity from these organisms averaged 18% and was in such small quantities that the metabolites were uncharacterizable. The only animal that contained Bux® was the crab (Uca manelensis) which had 0.0498 ppm and several other unidentified spots on the chromatogram. While the crab contained Bux®, nevertheless the extractable radioactivity only accounted for about 15% of the total radioactivity in the organism.

In contrast to the animals of this system, both the algae with 0.980 ppm and Elodea with 0.245 ppm contained considerable amounts of Bux®. While these two organisms contained substantial amounts of the parent compound, the unextractable radioactivity remained high as 81% and 73% in algae and Elodea, respectively, were acetone insoluble materials.

The water portion of the ecosystem contained small amounts of Bux® with a value of 0.0000953 ppm for the combined total of unhydrolyzed and hydrolyzed water. In addition to the Bux® there were several unidentified metabolites in the water. The unextractable radioactivity for the unhydrolyzed and hydrolyzed water was slightly higher at 94%.

Table 1

Concentrations (ppm) of Bux® and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Clam [b]	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
Bux®	0.98	0.980	--	0.0498	--	0.245	--	--	--
I [c]	0.95-0.62	0.474	--	0.168	--	0.107	--	--	--
II	0.62-0.28	0.252	--	0.056	--	0.206	--	--	--
III	0.28-0.02	0.074	--	0.0079	--	0.119	--	--	--
IV	0.00	0.00111	--	0.00508	--	0.268	--	--	--
Extractable ^{14}C		1.783	0.0206	0.287	0.128	0.945	0.0449	0.178	0.119
Unextractable ^{14}C		7.825	0.0826	1.59	1.42	2.51	0.230	0.602	0.662
Grand Total ^{14}C		9.608	0.103	1.877	1.548	3.455	0.275	0.780	0.781

[a] Microfiber absorbent sheets impregnated with silica gel, acetone-n-hexane, 15:85 by volume
[b] Clam died 7 days after application of Bux® to system
[c] Roman numerals - unknown spots

Table 2

Concentrations (ppm) of Bux® and metabolites in water of a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
Bux®	0.98	0.0000908	0.00000459
I [b]	0.95-0.62	0.0000454	0.0000360
II	0.62-0.28	0.00000258	0.0000126
III	0.28-0.02	--	0.0000589
IV	0.00	0.000000090	0.000103
Extractable ^{14}C		0.00014	0.000215
Unextractable ^{14}C		0.00281	0.00288
Grand Total ^{14}C		0.00295	0.00311

[a] Microfiber absorbent sheets impregnated with silica gel, solvent: acetone-n-hexane, 15:85 by volume

[b] Roman numerals - unknown spots

In summary, it can be concluded from the data obtained from the examination of Bux® in the model ecosystem that this carbamate insecticide does not accumulate in any of the animals of the system, though it appears to be concentrated from the water by the algae and Elodea, 10,283x and 2,571x, respectively. This phenomenon is peculiar in that this substantial accumulation does not appear to cause any damage to these plants. The probable explanation for the absence of Bux® in either the fish or mosquito relates to the water instability of this material. The program of operation of this system places these two organisms in the system on the 27th day for the mosquito and the 30th day for the fish, and by this time the Bux® has undergone hydrolysis to the phenol.

Sevin®

Sevin®, or carbaryl, was the first commercial carbamate insecticide to find widespread use in the early 1950's. Consequently, because of its extensive use, the metabolism of this insecticide has been thoroughly examined by numerous investigators and an adequate review of the metabolism and degradation of Sevin® has been outlined (Fukuto and Sims, 1971). Briefly, the primary routes of metabolism are ring hydroxylation, hydrolysis to yield α-napthol and transformation of the N-methylcarbamoyl group to the N-hydroxymethyl group.

Examination of the data in Table 3 gives clear evidence that this carbamate insecticide is similar to Bux® in its metabolic and degradative behavior in this system. While all of the organisms contained substantial radioactivity, none of the organisms contained carbaryl. The quantity of unextractable radioactivity in the organisms was on the average about 78%, which was slightly lower than that obtained for Bux®.

The aqueous segment of the ecosystem did not contain any carbaryl, but two identifiable metabolites in ppt concentrations were found; namely, N-hydroxymethyl carbaryl at 88 ppt and 7-OH carbaryl at 99 ppt. Other metabolites were co-chromatographed with the extract from water, but the radioactive spots did not correspond with any of the known compounds. Again, as in the case of Bux®, substantial amounts of unextractable radioactivity (72%) were found in the water. The greater susceptibility of carbaryl to undergo degradation to the numerous degradation products isolated from the water perhaps can be ascribed to the lower aromatic character of the napthalene ring which allows facile hydroxylation to polar, water soluble metabolites.

Carbofuran

The last carbamate investigated in the present study is carbofuran, an outstanding soil insecticide used for control of insects which affect corn. It was of particular importance to examine this insecticide in relation to the state of Illinois as nearly 40% of the corn in 1972 was treated with either an organic phosphate or carbamate (Kuhlman and Cooley, 1973). Further, since aldrin, heptachlor and chlordane were not recommended for use in Illinois to control insects which are pests

Table 3

Concentrations (ppm) of ring-labelled ^{14}C carbaryl and metabolites in organisms and water of a model ecosystem

Compound	R_f [a/]	Water	Algae	Clam	Crab	Daphnia	Elodea	Mosquito	Fish	Snail
I	0.95	--	0.175	--	0.118	--	0.057	--	--	0.03
II	0.87	0.000161	--	--	--	--	--	--	--	--
carbaryl	0.85	--	--	--	--	--	--	--	--	--
III	0.83	0.000155	--	--	--	--	--	--	--	--
A	0.79	--	--	--	--	--	--	--	--	--
IV	0.67	0.000221	--	--	--	--	--	--	--	--
V	0.53	0.00006	--	--	--	--	--	--	--	--
VI	0.47	0.000133	--	--	--	--	--	--	--	--
B	0.35	0.000081	--	--	--	--	--	--	--	--
C	0.30	--	--	--	--	--	--	--	--	--
D	0.26	--	--	--	--	--	--	--	--	--
VII	0.22	0.000018	--	--	--	--	--	--	--	--
E	0.18	0.000099	--	--	--	--	--	--	--	--
VIII	0.12	0.000765	--	--	0.0098	--	0.085	--	--	0.86

Table 3 (con't.)

Compound	R_f [a/]	Water	Algae	Clam	Crab	Daphnia	Elodea	Mosquito	Fish	Snail
IX	0.08	0.00151	--	--	0.0137	--	0.039	--	--	--
X	0.00	0.00748	0.614	--	0.257	--	0.909	--	0.091	0.45
Extractable ^{14}C		0.0107	0.789	0.286	0.398	0.295	1.089	0.360	0.091	1.34
Unextractable ^{14}C		0.0267	3.964	1.341	0.738	2.385	3.511	2.657	0.337	3.79
Grand Total ^{14}C		0.0374	4.753	1.627	1.136	2.681	4.600	3.017	0.428	5.13

∞

a/ Silica Gel GF-254, chloroform-methanol, 49:1 by volume
b/ Roman numerals - unknown spots
A 1-napthol
B N-hydroxymethyl carbaryl
C 5-hydroxy carbaryl
D 4-hydroxy carbaryl
E 7-hydroxy carbaryl

of corn (Kuhlman, 1973), it is clear that substitutes must be found, such as carbofuran. It was therefore paramount that this insecticide be examined in terms of its persistence and uptake by the organisms of this model ecosystem. An additional factor, which made it essential that this insecticide be examined, is its extreme toxicity to warm-blooded animals as it has an oral LD_{50} for the rat of 4 mg/kg (Metcalf, 1971).

Substantial work has been carried out on the metabolism of carbofuran and it has been adequately reviewed (Fukuto and Sims, 1971). The basic scheme of metabolism in plants and animals is oxidation of the 3-carbon to yield 3-hydroxy and 3-ketocarbofuran. Additional sites of metabolism involve aromatic hydroxylation and modification of the N-methylcarbamoyl moiety to give N-hydroxymethyl carbofuran. Environmental studies in soil have shown that carbofuran is hydrolyzed to yield the phenol, 2,3-dihydro-7-hydroxy-2,2-dimethylbenzofuran. The half-life for the transformation of the carbamate to the phenol was determined to be about 30 days. After the transformation of carbofuran to the phenol, the phenol becomes an unextractable residue with a half-life for extractability of about 7 days (Knaak, 1971).

Examination of the data in Tables 4 and 6 for carbofuran and its degradation products reveals that none of the organisms contained residues of carbofuran. In the carbonyl labeled carbofuran there were several unknown compounds isolated from Elodea as well as 3-ketocarbofuran (0.035 ppm), N-hydroxymethyl carbofuran (0.035 ppm) and 3-hydroxycarbofuran (0.0118 ppm). While there were not as many metabolites isolated from the ring-labeled carbofuran, Elodea contained small amounts of carbofuran phenol, 3-hydroxycarbofuran as well as a small amount of an unknown material which had an R_f of 0.36. Again, as previously observed for Bux® and Sevin®, most of the radioactivity for carbofuran was unextractable by acetone as values for ring- and carbonyl-labeled carbofuran were 69% and 77%, respectively. These high figures appear to be characteristic of carbamates in general and indicate their susceptibility to undergo degradation or metabolism to polar, uncharacterizable, unextractable species.

In the water portion of the carbonyl-labeled carbofuran ecosystem (Table 7) small amounts (0.000538 ppm) of the unchanged insecticide were isolated from the system. In comparison in the ring-labeled system (Table 5) the tlc resolution was not as precise because carbofuran and 3-ketocarbofuran phenol overlapped. However, there cannot be more than 0.00128 ppm of carbofuran, if it is assumed that the entire spot is carbofuran. Other spots found in identifiable quantities were 3-ketocarbofuran, N-hydroxymethyl carbofuran, carbofuran phenol and 3-hydroxy carbofuran. None of these compounds was found in excess of 10 ppt which indicates conclusively that carbofuran degrades to polar, water soluble materials which do not persist in the water segment of the ecosystem or remain at high levels.

Table 4

Concentrations (ppm) of ring-labeled carbofuran and metabolites in organisms of a model ecosystem

Compound	R_f[a]	Algae	Clam	Daphnia	Elodea	Fish	Frog	Mosquito	Snail
I[b]	0.98	--	--	--	--	0.0462	0.197	0.418	0.567
A	0.83	--	0.0130	--	--	0.000304	--	--	0.377
B and carbofuran	0.76	--	--	--	--	--	--	--	--
C	0.70	--	--	--	--	--	--	--	--
D	0.60	--	--	--	--	--	--	--	--
E	0.53	--	--	--	--	--	--	--	--
F	0.46	--	--	--	--	0.00526	--	--	--
II	0.36	--	--	--	--	0.000828	--	--	--
III	0.28	--	0.191	--	--	--	--	--	--
IV	0.13	--	--	--	--	--	--	--	--
V	0.06	--	--	--	--	--	--	--	--
VI	0.00	--	0.883	--	--	0.0216	0.305	0.552	0.890
Extractable ^{14}C		0.815	1.087	1.089	2.697	0.0725	0.502	1.071	1.645
Unextractable ^{14}C		4.648	0.368	4.690	2.993	0.413	1.034	4.835	6.270
Grand Total ^{14}C		5.463	1.455	5.779	5.689	0.485	1.536	5.906	7.915

Table 4 (con't.)

a/ Microfiber absorbent sheets impregnated with silica gel, solvent system: acetone-n-hexane, 15:85 by volume

b/ Roman numerals - unknown spots

A Carbofuran phenol

B Carbofuran and 3-ketocarbofuran phenol

C 3-ketocarbofuran

D 3-hydroxy carbofuran phenol

E N-hydroxymethyl carbofuran

F 3-hydroxy carbofuran

Table 5

Concentrations (ppm) of ring-labeled carbofuran and metabolites in water of a model ecosystem

Compound	R_f [a/]	Unhydrolyzed Water	Hydrolyzed Water
I [b/]	0.98	0.000267	0.000762
A	0.83	0.00884	0.00287
B and carbofuran	0.76	0.000909	0.000375
C	0.70	0.000136	0.000423
D	0.60	0.0000758	0.000280
E	0.53	0.000121	0.000242
F	0.46	0.000196	0.000415
II	0.36	0.000537	0.00255
III	0.28	0.000537	0.00143
IV	0.13	0.000137	0.00259
V	0.06	0.000230	0.00308
VI	0.00	0.000493	0.0166
Extractable ^{14}C		0.0037	0.0316
Unextractable ^{14}C		0.111	0.0652
Grand Total ^{14}C		0.115	0.097

a/ Microfiber absorbent sheets impregnated with silica gel, solvent system: acetone-n-hexane, 15:85 by volume

b/ Roman numerals - unknown spots

A Carbofuran phenol

B Carbofuran and 3-ketocarbofuran phenol

C 3-ketocarbofuran

D 3-hydroxy carbofuran phenol

E N-hydroxymethyl carbofuran

F 3-hydroxy carbofuran

Table 6

Concentrations (ppm) of carbonyl-labeled carbofuran and metabolites in organisms of a model ecosystem

Compound	R_f[a]	Algae	Clam	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
I[b]	0.96	--	--	0.121	--	0.0492	--	0.221	0.648
II	0.86	--	--	--	--	0.1261	--	--	--
III	0.75-0.71	--	--	--	--	0.0309	--	--	--
carbofuran	0.73	--	--	--	--	--	--	--	--
A	0.63	--	--	0.064	--	0.0350	--	--	--
B	0.55	--	--	--	--	0.0364	--	--	--
IV	0.51	--	--	--	--	0.0059	--	--	--
C	0.48	--	--	0.038	--	0.0118	--	--	--
V	0.26-0.00	--	--	--	--	0.5025	--	--	--
VI	0.00	--	--	0.0482	--	0.342	--	0.088	0.325
Extractable ^{14}C		0.963	0.02065	0.271	0.191	1.145	0.0583	0.435	0.972
Unextractable ^{14}C		3.000	0.100	0.254	1.092	4.835	0.278	1.198	6.518
Grand Total ^{14}C		3.963	0.12065	0.525	1.283	5.980	0.3363	1.583	7.490

Table 6 (con't.)

a/ Microfiber absorbent sheets impregnated with silica gel, solvent: acetone-n-hexane, 15:85 by volume

b/ Roman numerals - unknown spots

A 3-ketocarbofuran

B N-hydroxymethyl carbofuran

C 3-hydroxy carbofuran

Table 7

Concentrations (ppm) of carbonyl-labeled carbofuran and metabolites in water of a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
I [b]	0.96	0.00000491	0.0000070
II	0.86	0.0000136	0.000110
III	0.75-0.71	--	--
carbofuran	0.73	0.000364	0.000174
A	0.63	0.00000859	0.000650
B	0.55	0.00000747	0.0000246
IV	0.51	--	--
C	0.48	0.00000128	0.0000246
V	0.26-0.00	0.00000464	0.000073
VI	0.00	0.0000103	0.000756
Extractable ^{14}C		0.000415	0.00178
Unextractable ^{14}C		0.00374	0.00259
Grand Total ^{14}C		0.00416	0.00437

[a] Microfiber absorbent sheets impregnated with silica gel, solvent: acetone-n-hexane, 15:85 by volume

[b] Roman numerals - unknown spots

A 3-ketocarbofuran

B N-hydroxymethyl carbofuran

C 3-hydroxy carbofuran

At this point it may be suitable to make some general comments about the previous three compounds and their behavior in this terrestrial-aquatic model ecosystem. All three were carbamate insecticides and were shown to be nonpersistent and did not accumulate in any of the organisms of this system. This property may be characteristic of all aryl carbamate insecticides as they have sites for oxidative metabolism, namely, the ring, the N-methyl group and aliphatic side chains. In addition to these sites, which are susceptible to oxidative metabolism, the carbamoyl group can undergo hydrolysis to a phenol which detoxifies the carbamate and provides a moiety which can be conjugated with sugars, phosphate or sulfate. If the data obtained for these carbamates in this model ecosystem is representative of the behavior of aryl N-methyl carbamate insecticides, then it would appear that the use of these insecticides will not present ecological problems related to persistence and food chain accumulation.

Dieldrin

The next pesticide to be discussed is the chlorinated hydrocarbon, dieldrin. The unoxidized precursor to dieldrin, aldrin, was introduced about 20 years ago as an effective insecticide for the control of soil insects, particularly those associated with corn. The continual use of this material for over 20 years has resulted in resistance to this insecticide and, therefore, the aldrin/dieldrin treatment of corn insects is not particularly effective for some corn pests (Sechriest and Sherrod, 1973). The increased emphasis on environmental quality has also suggested the discontinued use of aldrin and/or dieldrin as dieldrin, the oxidation product of aldrin, is very persistent with a soil half-life of about 3 years (Wingo, 1968; Hurtig, 1972). The persistence is related to the extreme inertness toward chemical or biological modification. For example, metabolism studies with dieldrin and wheat (Saha, 1970) indicated that less than 3% of the application of dieldrin was transformed into metabolites. This corroborates earlier work done with corn, alfalfa and orchard grass that dieldrin does not undergo substantial transformation by these plants (Wheeler et al., 1967).

The inert nature of dieldrin to undergo degradation in plants is contrasted by metabolic susceptibility when administered orally to a variety of mammals. For example, 70% of the oral dose to rats is eliminated, principally via the feces which points to biliary excretion (Heath and Vandekar, 1964). More recently, the structure of the principal metabolite from an oral dose to rats has been identified as 6,7-trans-dihydroxydihydro aldrin with a specific rotation of $[\alpha]_D^{20}$ + 13.7°.

The data in Tables 8 and 9 for dieldrin in the model ecosystem demonstrate the inert nature of dieldrin to undergo biological or chemical degradation. There was dieldrin in every organism in the ecosystem ranging from a low of 0.495 ppm in the crab (Uca manilensis) to 230 ppm in the snail. Even more important is that dieldrin constituted nearly

Table 8

Concentrations (ppm) of dieldrin and metabolites in organisms of a model ecosystem

Compound	R_f[a/]	Algae	Clam	Crab	Daphnia	Elodea	Mosquito	Fish	Snail
I[b/]	0.65	--	--	--	--	0.23	--	--	0.866
dieldrin	0.58	14.96	2.03	0.495	5.07	2.56	--	12.29	229.87
II	0.43	--	--	--	--	--	--	--	0.456
A	0.38	0.20	--	--	--	--	--	0.19	1.11
B	0.31	--	--	0.043	--	--	--	0.07	--
VII	0.00	--	--	--	0.07	0.03	--	0.03	0.044
Extractable ^{14}C		15.16	2.03	0.536	5.14	2.82	1.35	12.57	232.3
Unextractable ^{14}C		1.23	0.028	0.177	0.10	0.14	0.25	0.65	1.78
Grand Total ^{14}C		16.39	2.06	0.715	5.24	2.96	1.60	13.22	234.1

a/ Silica Gel GF-254, ether-n-hexane, 3:2 by volume
b/ Roman numerals - unknown spots
A 9-hydroxy dieldrin
B 9-keto dieldrin

Table 9

Concentrations (ppm) of dieldrin and metabolites in water of a model ecosystem

Compound	R_f [a/]	Unhydrolyzed Water	Hydrolyzed Water
dieldrin	0.58	0.0020	--
A	0.38	0.00046	--
B	0.31	0.00040	--
III [b/]	0.18	0.00034	--
IV	0.12	0.00013	0.00012
V	0.07	0.00012	0.00023
VI	0.04	0.00093	0.00108
VII	0.00	0.00023	0.00134
Extractable ^{14}C		0.0046	0.0028
Unextractable ^{14}C		0.0028	--
Grand Total ^{14}C		0.0074	--

a/ Silica Gel GF-254, ether-n-hexane, 3:2 by volume
b/ Roman numerals - unknown spots
A 9-hydroxy dieldrin
B 9-keto dieldrin

88% of the total radioactivity isolated from the organisms. This figure includes both extractable and unextractable radioactivity. Clearly, dieldrin is not metabolized to polar, water soluble molecules by the organisms of the system, nor is it degraded by physical or chemical processes as little of the radioactivity isolated from the organisms (∿9%) is unextractable. This figure contrasts significantly with that observed for the three carbamate insecticides (∿65-75%) or the phosphates (∿60-70%) which will be reviewed next. In view of the low, mixed-function oxidase levels of Gambusia affinis (Krieger and Lee, 1972) and Physa (Metcalf et al., 1971), it is not surprising that dieldrin is accumulated by these organisms as they appear to be incapable of transforming the lipid soluble molecule, dieldrin, into water soluble metabolites.

The distribution of degradation products of dieldrin in the water (Table 9) differs slightly from the distribution in the organisms as dieldrin constitutes only 25-28% of the extractable radioactivity. Furthermore, dieldrin is in lower concentration (0.0020 ppm) than was isolated from the organisms. The reduced amount of dieldrin in the water, as compared with organisms, is probably related to the low water solubility, 0.25 ppm (Gunther et al., 1968). If the amount of dieldrin isolated from the water is divided into the various concentrations of dieldrin observed in the organisms, then the tendency for dieldrin to accumulate in the various organisms can be calculated. The concentration factors for the snail, algae and fish are approximately 115,000, 7,500 and 6,100, respectively. These values compare satisfactorily with those obtained in the same ecosystem experiment with dieldrin where the factors were determined to be 61,657 and 2,700 for snail and fish, respectively (Metcalf et al., 1973). More importantly, the order of magnitude for accumulation of dieldrin by aquatic organisms has been observed to be in the same order of magnitude, particularly the fish of the model ecosystem, as that in fish collected from farm ponds in Illinois. For example, it has been observed that dieldrin is concentrated by several species of fish from 5,000x to 25,000x the concentration in the water (Childers and Bruce, 1973). This would again appear to validate the usefulness of the model ecosystem to predict the behavior of pesticides in the aquatic environment.

Lindane and Aroclor 5460® (1:5 w/w)

The types and variations of experiments that can be carried out in this terrestrial-aquatic ecosystem are only limited by the imagination of the investigator. In the experiment with lindane and this polychlorinated terphenyl, the intended purpose was to examine the effect that this adjuvant might have on the persistence and fate of lindane in the model ecosystem. This type of experiment is not without precedence as it has been previously reported that persistence and insecticidal residues of lindane could be improved by the addition of Aroclor 5460® (Horstein et al., 1953; Lichtenstein, 1969). It was concluded that residues of lindane and Aroclor 5460® were more persistent because of the retardation of the evaporation rate of lindane from treated surfaces

(Tsao, 1953). Further, impetus for conducting this type of paired interaction experiment is given by the dearth of information under controlled environmental conditions of studies involving interactions of chemicals and the effects that an adjuvant, such as Aroclor 5460®, may have on the environmental persistence of a pesticide.

The fate of lindane alone in this model ecosystem has been investigated which makes it possible to compare the effect of this plasticizer on the persistence of lindane (Metcalf et al., 1973). Further, the metabolism of lindane in plants and animals has been adequately reviewed (Fukuto and Sims, 1971). The initial transformation which results in inactivation of lindane is a dehydrohalogenation to yield pentachlorocyclohexene. This unsaturated chlorinated cyclohexene undergoes further transformations to form conjugates with glutathione and dechlorination to form several isomeric chlorinated phenols.

Examination of the data in Table 10 for the distribution of lindane in the organisms of the model ecosystem shows that lindane is present in all organisms ranging from about 2.20 ppm for Daphnia to about 26.40 ppm for the fish. The value for the fish is about 26x greater than the value found by Metcalf et al. (1973), which would indicate that the addition of the terphenyl increases the uptake of lindane by the fish. However, the variability in concentrations of lindane in the two fish from the duplicate experiments was unusually high, 48.98 ppm and 3.78 ppm, and therefore, to make an absolute statement about the accumulation of lindane to be about 28x greater in the presence of Aroclor 5460® would be tenuous. It can be stated that there was a subtle effect of the plasticizer as identifiable amounts of lindane were found in the present experiment in the algae, 6.18 ppm; Daphnia, 2.17 ppm; snail, 5.66 ppm and mosquito, 4.21 ppm. Without the Aroclor 5460®, no lindane was found in the algae or mosquito, but substantial amounts were found in the snail, 0.762 ppm, and fish, 0.975 ppm (Metcalf et al., 1973). Clearly, this preliminary experiment with lindane and Aroclor 5460® demonstrates the potentiality for studying the interactions of compounds. In a recent investigation it has been demonstrated that piperonyl butoxide (pb), an insecticide synergist, will increase both the total radioactivity in the snail and fish as well as the concentration of methoxychlor in these two organisms (Metcalf, 1973).

Other data of interest in the metabolite distribution from the organisms is that neither of the two chlorinated phenols, 2,4,6-trichlorophenol or 2,4,5-trichlorophenol, were found in the organisms, while small amounts were found in the water which will be discussed next. These two chlorinated phenols have been reported as urinary excretion products when rats were fed lindane (Grover and Sims, 1965). A final point that should be made is the low percentage of unextractable radioactivity (average 7%) in the organisms. This figure is similar to the value for dieldrin and about one-tenth of the amount obtained for the carbamate and phosphate insecticides. The data for the previous experiment with lindane in this model ecosystem also indicate a low amount of unextractable radioactivity, which would seem to imply that the addition of the

Table 10

Concentrations (ppm) of lindane and Aroclor 5460® and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Daphnia	Fish	Mosquito	Snail
A	0.75	--	--	0.025	--	--
lindane	0.40	6.178	2.166	26.379	4.212	5.658
B	0.19	--	--	--	--	--
C	0.13	--	--	--	--	--
I [b]	0.06	--	--	--	--	0.110
II	0.00	0.285	0.127	1.004	0.108	0.410
Extractable ^{14}C		6.463	2.293	27.408	4.320	6.178
Unextractable ^{14}C		0.803	0.164	0.087	0.309	0.522
Grand Total ^{14}C		7.266	2.457	27.495	4.629	6.700

[a] Silica Gel GF-254, petroleum ether-carbon tetrachloride, 1:1 by volume
[b] Roman numerals - unknown spots
A pentachlorocyclohexene
B 2,4,6-trichlorophenol
C 2,4,5-trichlorophenol

Table 11

Concentrations (ppm) of lindane and Aroclor 5460® and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
A	0.75	0.0000608	--
lindane	0.40	0.0125	--
B	0.19	0.000471	0.000056
C	0.13	0.000418	0.000182
I [b]	0.06	0.000433	0.000352
II	0.00	0.00124	0.00144
Extractable ^{14}C		0.01520	0.00202
Unextractable ^{14}C		0.00740	0.00430
Grand Total ^{14}C		0.0226	0.00632

[a] Silica Gel GF-254, pet ether-carbon tetrachloride, 1:1 by volume
[b] Roman numerals - unknown spots
A pentachlorocyclohexene
B 2,4,6-trichlorophenol
C 2,4,5-trichlorophenol

polychlorinated terphenyl does not affect the metabolism of lindane to polar, unextractable metabolites.

The distribution of metabolites in the water (Table 11) for this experiment of lindane and Aroclor 5460® is somewhat different than if lindane is put through the system alone. The most striking difference is the greater quantity of lindane, 0.0126 ppm, found in the present experiment as compared to 0.00167 ppm (Metcalf et al., 1973), which is an increase of about 7.5x. Further, in the present experiment it was possible to identify small amounts of 2,4,6-trichlorophenol, 0.00053 ppm and 2,4,5-trichlorophenol, 0.0006 ppm. If the concentration of lindane isolated from the water is divided into the fish and snail, concentration factors are derived of ~2,100x and 448x, respectively. The value obtained for the fish is about 4x that obtained for the fish for lindane alone (Metcalf et al., 1973), while the snail value in the present experiment is nearly identical. The interaction of pesticides and other chemicals, such as a polychlorinated terphenyl, give results that are complex and difficult to interpret. Finally, the unextractable radioactivity from the water for the lindane experiment alone was about 2.5% (Metcalf et al., 1973), while the unextractable radioactivity from the present experiment amounted to 26%. The effect of Aroclor 5460® on the metabolism, degradation and persistence of lindane in the water is a 10-fold increase in unextractable radioactivity.

Orthene®

Orthene® is a new organophosphate insecticide which shows moderate persistence and a residual activity of 5-10 days. In field trials conducted from 1968 to 1972 this insecticide was effective in controlling pest species of aphids and lepidopterous larvae. In contrast to parathion, this phosphoramidothioate insecticide shows a low order of toxicity to higher animals as the LD_{50} to male rats is about 945 mg/kg, which is about 100x less toxic than parathion. In addition, the 96-hr TL_{50} for Orthene® is greater than 1,000 ppm for trout, 1,725 ppm for large-mouth bass, 2,050 ppm for blue gill, 2,230 for channel catfish, 6,650 for mosquito fish (Gambusia) and 9,550 ppm for goldfish. The preceding data, which was taken from the technical data sheet available from the Chevron Chemical Company (1972) indicates that this material is safe in terms of acute toxicity to both fish and mammals.

The metabolism pathways of this insecticide have not been published, but a number of possibilities for potential metabolites and/or degradation products can be hypothesized. The loss of the N-acetyl group to give O,S-dimethyl phosphoramidothioate, another Chevron Chemical Company product, Monitor®, is an obvious metabolite as similar transformations are known to occur from metabolism studies on N-derivatized carbamates (Miskus et al., 1969). This transformation to Monitor® results in a more toxic molecule to the rat as the LD_{50} of this compound is 18.9 mg/kg (Chevron Chemical Company, 1972). Another transformation that Orthene® might undergo is cleavage of either the S-methyl or O-methyl moieties to yield the S-methyl acetamidophosphorothioic acid or

O-methyl acetamidophosphoric acid, respectively. The cleavage of either S-methyl or O-methyl could occur after loss of the acetyl moiety from nitrogen to yield either O-methyl phosphoramidic acid or S-methyl phosphoramidothioic acid. One final transformation that could occur is the removal of the amino group after loss of the acetyl group to yield O,S-dimethyl phosphorothioic acid.

Examination of the data in Tables 12 and 13 for the organisms and water, respectively, shows that none of the chromatographed metabolites were found in identifiable quantities in the organisms. An unusual occurrence was the formation of a degradation product which was less polar than Orthene®, which had an R_f of 0.70, or Monitor®, which had an R_f of 0.79. This metabolite varied in concentration from about 0.26 ppm in Daphnia to greater than 2.0 ppm in the crab. Since the site of the label was ^{14}C S-methyl, perhaps this nonpolar species is not related to Orthene®, but has been utilized as a source of carbon in a structural entity in the organism from which it was isolated.

Finally, as was previously indicated for the carbamate insecticide, the unextractable radioactivity in the organisms for Orthene® was high at about 72%. This indicates that this insecticide breaks down over the time period of the model ecosystem to nonlipid—partitioning products. The only product which appears in the organisms is nonpolar (R_f, 0.93) and does not appear to be deleterious. It is not surprising to find that Orthene does not accumulate in the organisms of this system as the water solubility of this insecticide is reported to be about 650,000 ppm (Chevron Chemical Company, 1972).

In the water of this model ecosystem (Table 13) were small amounts of Orthene®, 0.000282 ppm, and as well as small quantities (0.000478 ppm) of the unknown which was nonpolar and had an R_f value of 0.93. This nonpolar species was accumulated from the water by the various organisms from 538x for Daphnia to about 4,300x for the crab. Trace amounts of Monitor®, 0.000124 ppm, and the ammonium salt of S-methyl acetylphosphoramidothioate, 0.000015 ppm, were found in the hydrolyzed water. Finally, the high value found for the unextractable radioactivity in unhydrolyzed water, >99%, and hydrolyzed water, ~97%, indicates the susceptibility of Orthene® to undergo degradation to metabolites of high water solubility.

Parathion

Parathion is a member of the first generation of organophosphorus insecticides used in the United States. It was originally discovered in Germany by Gerhard Schrader during World War II and since then has been used for the control of insects which are pests of many crops. The large-scale use of parathion is indicated by the 15,259,000 pounds manufactured in the United States in 1970. While there does not seem to be environmental problems associated with the use of parathion, nevertheless it is paramount that insecticides that are highly toxic to warm-blooded animals (oral LD_{50}, rats 4-13 mg/kg) be examined to

Table 12

Concentrations (ppm) of Orthene® and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Clam	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
I [b]	0.93	0.936	--	2.038	0.257	0.408	--	0.797	0.796
A	0.79	--	--	--	--	--	--	--	--
Orthene®	0.70	--	--	--	--	--	--	--	--
B	0.45	--	--	--	--	--	--	--	--
C	0.33	--	--	--	--	--	--	--	--
II	0.25	0.0538	--	--	--	--	--	--	--
III	0.11	0.0142	--	--	--	0.00280	--	--	--
IV	0.00	0.0395	--	0.247	0.143	0.0098	--	0.0247	0.130
Extractable ^{14}C		1.043	0.100	2.284	0.400	0.421	0.0309	0.822	0.927
Unextractable ^{14}C		3.517	0.148	3.631	1.979	1.435	0.0621	2.466	2.769
Grand Total ^{14}C		4.560	0.248	5.915	2.379	1.856	0.0930	3.288	3.696

[a] Silica Gel GF-254, aluminum plate in 15% acetic acid in benzene-propanol, 1:1 by volume
[b] Roman numerals - unknown spots
A O,S-dimethyl phosphoramidothioate
B O,S-dimethyl phosphorothioate sodium salt
C S-methyl N-acetylphosphoramidothioate ammonium salt

Table 13

Concentrations (ppm) of Orthene® and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
I [b]	0.93	0.0000617	0.000416
A	0.79	--	0.000124
Orthene®	0.70	0.0000484	0.000234
B	0.45	--	--
C	0.33	--	0.0000150
II	0.25	--	--
III	0.11	--	--
IV	0.00	--	0.0000255
Extractable ^{14}C		0.00011	0.00082
Unextractable ^{14}C		0.0376	0.0236
Grand Total ^{14}C		0.0377	0.0244

[a] Silica Gel GF-254, aluminum plate in 15% acetic acid in benzene-propanol, 1:1 by volume

[b] Roman numerals - unknown spots

A O,S-dimethyl phosphoramidothioate

B O,S-dimethyl phosphorothioate sodium salt

C S-methyl N-acetylphosphoramidothioate

determine their persistence in the model ecosystem. Further, the investigation of pesticides in this model ecosystem, such as parathion which has had widespread use without apparent accumulation in food chains, is necessary so that field and model ecosystem data can be compared to test the validity of the model ecosystem as a screening test for pesticide persistence.

The metabolism of parathion has been thoroughly studied in animals and somewhat less detailed studies have been carried out in plants and soil. Briefly, the major alterations of parathion are oxidation to paraoxon and cleavage of parathion to diethylphosphorothioic acid and p-nitrophenol. Paraoxon can undergo O-dealkylation to O-ethyl, O-p-nitrophenyl phosphoric acid as well as cleavage to diethyl phosphoric acid and p-nitrophenol.

The model ecosystem study with parathion demonstrates the rapid breakdown of this insecticide as the data in Tables 14 and 15 show that this phosphate does not persist to any great extent nor does it accumulate in the fish as was observed for the chlorinated hydrocarbon, dieldrin. Only the fish (0.100 ppm) contained parathion as all the other organisms had neither parathion, paraoxon nor p-nitrophenol. Therefore, it was possible to establish the fate of p-nitrophenol since the site of the ^{14}C label was in the 2,6-positions of this moiety. It would seem important to establish the fate of p-nitrophenol and other phenols in a model ecosystem as they are significant constituents of a number of organophosphorus insecticides. Again as previously discussed for the phosphate insecticide, Orthene®, and the three carbamates in this report, substantial amounts of the radioactivity, with the exception of the fish, was unextractable (average 65%). An explanation for the relatively high amounts of extractable radioactivity (81%) in the fish is the low microsomal activity in the liver of Gambusia (Krieger and Lee, 1973) which does not metabolize parathion to polar, unextractable products.

The water segment (Table 15) of the ecosystems contains small amounts of parathion, 0.0003 ppm; paraoxon, 0.00047 ppm; and p-nitrophenol, 0.00095 ppm. In addition, there were small amounts of unknown metabolites which had R_f values of 0.97, 0.73, 0.33, 0.09, 0.13 and 0.00. The accumulation of parathion by the fish over the concentration in the water was about 335x, which is about 0.054 the value observed for dieldrin in this model ecosystem. Probably, the higher water solubility of parathion, 25 ppm (Gunther et al., 1968), as compared to dieldrin, 0.25 ppm (Gunther et al., 1968), and the greater susceptibility of parathion to undergo degradation account for the substantially less concentration of parathion by the fish in this model ecosystem. The portion of unextractable radioactivity in the water was smaller than for Orthene®, as it averaged about 40%. Perhaps this decrease from approximately 98-99% for Orthene® indicates that parathion, as compared to Orthene®, is less degradable and therefore more persistent in the aqueous compartment of this model ecosystem.

Table 14

Concentrations (ppm) of parathion and metabolites in organisms of a model ecosystem

Compound	R_f [a]	Algae	Daphnia	Fish	Mosquito	Snail
I [b]	0.97	0.0356	--	--	--	--
parathion	0.90	--	--	0.1006	--	--
A	0.55	--	--	0.0086	--	--
III	0.33	--	--	0.0222	--	--
VI	0.00	0.3613	0.2987	0.0621	0.2031	0.2701
Extractable ^{14}C		0.3969	0.2987	0.1935	0.2031	0.2701
Unextractable ^{14}C		2.6284	0.3126	0.2055	0.4685	0.5813
Grand Total ^{14}C		3.0253	0.6113	0.3990	0.6716	0.8518

a/ Silica Gel GF-254, diethyl ether-n-hexane, 7:3 by volume
b/ Roman numerals - unknown spots
A p-nitrophenol

Table 15

Concentrations (ppm) of parathion and metabolites in water of a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
I [b]	0.97	0.00020	--
parathion	0.90	0.00030	--
II	0.73	0.00006	--
p-NO_2phenol	0.55	0.00074	0.00062
III	0.33	0.00018	0.00007
paraoxon	0.25	0.00031	0.00016
IV	0.13	0.00049	--
V	0.09	0.00151	0.00123
VI	0.00	0.00222	0.00377
Extractable ^{14}C		0.00661	0.00585
Unextractable ^{14}C		0.0144	0.00853
Grand Total ^{14}C		0.0210	0.01438

[a] Silica Gel GF-254, ether-hexane, 7:3 by volume
[b] Roman numerals - unknown spots

SECTION IV

EXAMINATION OF SELECT HERBICIDES

The second aspect of this report is concerned with the fate of several herbicides in this model ecosystem. While the acute toxicity of most herbicides to mammals is low, it still is necessary to derive information which can be used as a predictive measure of the potential for these pest chemicals to accumulate and persist in the environment. Therefore, the next section should provide information about several members of this class of pesticide chemicals. It is hoped that additional herbicides can be examined in this system, particularly those which currently have a widespread use, so that a baseline can be established for the comparison of new herbicides.

Alachlor and Propachlor

Since alachlor and propachlor have similar structures chemically, namely, 2-chloroacetanlides, the discussion of these two compounds and their behavior in the model ecosystem will be combined. Both compounds are safe in terms of acute toxicity as the oral LD_{50} values for alachlor and propachlor are 1,200 mg/kg and 1,500 mg/kg, respectively. The soil persistence of these two herbicides is 1-2 months which is quite short. The principal use has been in the control of weeds in corn as preemergence, preplant or postemergence treatments. The mode of action of propachlor in susceptible plants appears to be the inhibition of utilization of proteinacous and lipid reserves which are necessary for plant growth (Dhillion, 1971).

Some work on the metabolism of these herbicides in soil and plants has been carried out, but it is by no means extensive. Laboratory studies in soil indicates the primary degradative route for alachlor is loss of the $-CH_2OCH_3$ moiety from nitrogen (Hargrove and Merkle, 1971). This transformation is believed to take place on the acidic soil surface. Higher relative humidity decreases the herbicide contact with the soil surface which then decreases the rate of this transformation. Metabolism of propachlor by corn, sorghum and sugarcane plants yields a conjugate of glutathione as a primary metabolite (Lamoreaux and Tanaka, 1971).

The data for these two herbicides for the organisms contained in Tables 16 to 19 reveal conclusively the lack of uptake of either of these two herbicides by any of the organisms. The water had numerous unidentified metabolites which were not in the organisms as well as small amounts of the parent compounds, 0.0564 ppb for propachlor and about 1.05 ppb for alachlor. The 2-chloro group of the acetanilde is a labile moiety and could undergo displacement to yield a substantially more water soluble moiety, though no metabolite was available for co-chromatography. In addition, as evidenced by the approximately 17 unidentified compounds, it can be stated that both of these herbicides are susceptible to degradation to water-soluble, nonlipid-partitioning organic compounds.

Table 16

Concentrations (ppm) of alachlor and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
I [b]	0.70	--	--	--	--	--	--	--
alachlor	0.61	--	--	--	--	--	--	--
II	0.51	--	--	--	--	--	--	--
III	0.43	--	--	--	--	--	--	--
IV	0.33	--	--	--	--	--	--	--
V	0.27	--	--	--	--	--	--	0.658
VI	0.20	--	--	--	--	--	--	--
VII	0.13	--	--	--	--	--	--	--
VIII	0.07	--	--	--	--	--	--	--
IX	0.00	--	--	--	--	--	--	0.185
Extractable ^{14}C		0.0898	0.321	0.000	1.767	0.125	0.0452	0.843
Unextractable ^{14}C		0.569	0.524	0.422	2.961	0.106	0.244	0.544
Grand Total ^{14}C		0.658	0.845	0.422	4.728	0.231	0.289	1.387

[a] Silica Gel GF-254, methanol-benzene, 5:95 by volume
[b] Roman numerals - unknown spots

Table 17

Concentrations (ppm) of alachlor and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
I [b]	0.70	0.000271	0.000677
alachlor	0.61	0.00105	--
II	0.51	0.00190	0.00154
III	0.43	0.0105	0.00364
IV	0.33	0.000777	0.00146
V	0.27	--	--
VI	0.20	0.000832	0.00854
VII	0.13	0.00172	--
VIII	0.07	0.000687	0.00300
IX	0.00	0.000362	0.00465
Extractable ^{14}C		0.0181	0.0212
Unextractable ^{14}C		0.0414	0.0118
Grand Total ^{14}C		0.0595	0.0330

[a] Silica Gel GF-254, methanol-benzene, 5:95 by volume
[b] Roman numerals - unknown spots

Table 18

Concentrations (ppm) of propachlor and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Clam	Daphnia	Elodea	Fish	Mosquito	Snail
I [b]	0.69	--	--	--	--	--	--	--
II	0.62	--	--	--	--	--	--	--
propachlor	0.55	--	--	--	--	--	--	--
III	0.40	--	--	--	--	--	--	--
IV	0.30	--	--	--	--	--	--	0.0154
V	0.27-0.15	--	--	--	--	--	--	--
VI	0.10	--	--	--	--	--	--	--
VII	0.03	--	--	--	--	--	--	--
VIII	0.00	--	--	--	--	--	--	0.0595
Extractable ^{14}C		0.0211	0.00619	0.00930	0.00243	0.00605	0.0264	0.0749
Unextractable ^{14}C		0.186	0.00886	0.0476	0.0869	0.00854	0.134	0.177
Grand Total ^{14}C		0.207	0.0150	0.0569	0.0893	0.0146	0.160	0.252

[a] Silica Gel GF-254, methanol-benzene, 5:95 by volume
[b] Roman numerals - unknown spots

Table 19

Concentrations (ppm) of propachlor and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
I [b]	0.69	--	0.0000622
II	0.62	0.0000614	0.000108
propachlor	0.55	0.0000564	--
III	0.40	0.00125	0.00193
IV	0.30	--	--
V	0.27-0.15	0.000144	0.000277
VI	0.10	0.0000830	0.000189
VII	0.03	0.0000216	0.000297
VIII	0.00	0.0000382	0.00390
Extractable ^{14}C		0.00166	0.00676
Unextractable ^{14}C		0.0121	0.00414
Grand Total ^{14}C		0.0138	0.0109

[a] Silica Gel GF-254, methanol-benzene, 5:95 by volume
[b] Roman numerals - unknown spots

Bladex®

Bladex® is a member of the s-triazine structural class of herbicides which has found use for the control of annual grasses and broadleaf weeds in corn as a preemergence treatment. The preemergence treatment for corn with Bladex® is preferred as injury often results when the herbicide is put on after the corn has emerged. Under normal agricultural usage (1-4 lb/A) the half-life varied between 2-7 weeks, while laboratory half-life on three typical soils was about 15 days. The toxicity to fish and birds is low, which correlates with the oral LD_{50} of 334 mg/kg obtained for rats.

The metabolism of Bladex® in rats (Hutson et al., 1970) and degradation in soil have been examined (Beynon et al., 1972). The principal metabolites in rat urine are the N-desethylated Bladex® and replacement of the 2-chloro group with an N-acetyl cysteine which is conjugated through a sulfur linkage. The degradation in the soil is more complicated as the nitrile is hydrolyzed to the amide and, finally, the acid. The Cl group is replaced by OH and also N-desethylation takes place.

The data for the distribution of Bladex® in the organisms and degradation products are contained in Table 20. With the exception of Elodea, which contained 0.621 ppm Bladex® and the crab with 0.172 ppm of the N-desethylated Bladex®, none of the other organisms had residues of identifiable metabolites. The organisms contained extractable radioactivity which ranged from a low of ∿0.02 ppm for Daphnia to a value of 0.629 ppm for Elodea. Significantly, of this 0.629 ppm isolated from the water plant, nearly 99% was intact Bladex®. The level of unextractable radioactivity from the organisms averaged 48%, indicating a substantial degree of degradation of this herbicide.

The water portion of this ecosystem (Table 21) is interesting in terms of the distribution of degradation products as several were present in indentifiable amounts along with Bladex® which was found at 3.2 ppb. Two others which were found were the amide at 1.42 ppb and the N-desethylated amide at 0.0568 ppb. In addition to these degradation products, there were several unidentified materials at levels of 0.014-0.028 ppt. Clearly, none of the metabolites isolated from the water appears in any of the organisms, which indicates that neither Bladex® nor any of its metabolites accumulate in the organisms of this model ecosystem.

Bentazon®

Bentazon® is a new herbicide that is being developed as a broadleaf weed control for application as a postemergence treatment. There is little published information about the metabolism of this herbicide or its behavior in the soil environment. Recently, a study was conducted to determine the affinity of Bentazon® for 12 Illinois soils and the data indicate that it does not bind tightly to any of them (Abernathy and Wax, 1973).

Table 20

Concentrations (ppm) of Bladex® and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
Bladex®	0.55	--	--	--	0.621	--	--	--
A	0.47	--	0.172	--	--	--	--	--
B	0.37	--	--	--	--	--	--	--
C	0.26	--	--	--	--	--	--	--
I [b]	0.16	--	--	--	--	--	--	--
II	0.07	--	0.0579	--	--	--	--	--
III	0.00	--	0.0812	--	0.00818	--	-	--
Extractable ^{14}C		0.129	0.311	0.0196	0.629	0.0354	0.0277	0.0454
Unextractable ^{14}C		0.127	0.209	0.0202	0.0253	0.0157	0.0751	0.0624
Grand Total ^{14}C		0.256	0.520	0.0398	0.654	0.0511	0.103	0.108

[a] Silica Gel GF-254, methanol-acetone-chloroform, 5:45:50 by volume
[b] Roman numerals - unknown spots
A 2-chloro-4-amino-6-(1-methyl-1-cyanoethylamino)-s-triazine
B 2-chloro-4-ethylamino-6-(1-methyl-1-carboxamidoethylamino)-s-triazine
C 2-chloro-4-amino-6-(1-methyl-1-carboxamidoethylamino)-s-triazine

Table 21

Concentrations (ppm) of Bladex® and metabolites in water in a model ecosystem

Compound	R_f [a/]	Unhydrolyzed Water	Hydrolyzed Water
Bladex®	0.55	0.00321	--
A	0.47	0.0107	--
B	0.37	0.000142	--
C	0.26	0.0000568	--
I	0.16	0.0000142	0.0000626
II	0.07	0.0000142	0.0000726
III	0.00	0.0000284	0.0000250
Extractable ^{14}C		0.0142	0.00016
Unextractable ^{14}C		0.00359	0.00357
Grand Total ^{14}C		0.0178	0.00373

a/ Silica Gel GF-254, methanol-acetone-chloroform, 5:45:50 by volume

b/ Roman numerals - unknown spots

A 2-chlor-4-amino-6-(1-methyl-1-cyanoethylamino)-s-triazine

B 2-chloro-4-ethylamino-6-(1-methyl-1-carboxamidoethylamino)-s-triazine

C 2-chloro-4-amino-6-(1-methyl-1-carboxamidoethylamino)-s-triazine

The data for the distribution of metabolites and degradation products of Bentazon® in the organisms of the model ecosystem are compiled in Table 22. The crab was the only organism that contained metabolites, including Bentazon® at 0.512 ppm, anthranilic acid at 1.27 ppm and N-isopropyl anthranilamide at 0.622 ppm. Most of the other organisms contained small amounts of ^{14}C labeled extractable metabolites that were in such low concentration identification was not possible.

The data for the degradation products in the water segment of the ecosystem are collected in Table 23. The water contained 0.0213 ppm of N-isopropyl anthranilamide and 0.0505 ppm of Bentazon®, but no anthranilic acid. Several metabolites and Bentazon® were accumulated from the water to a slight extent by the crab as both N-isopropyl anthranilamide and Bentazon® were higher in concentration in the crab than in the water.

Dicamba

Dicamba is an effective herbicide for numerous annual grasses and broadleaf weeds in grain crops. It is more persistent in the soil than 2,4-D which was essentially degraded in sandy loam and loam after two weeks; but dicamba after 12 weeks was still highly active (Friesen, 1965). Dicamba in high organic soils is detoxified rapidly at pH 5.3, but appears to be highly persistent at pH 7.5. An explanation for this is the increase proliferation of soil bacteria at the lower pH which are capable of degrading the herbicide (Swanson, 1969). This herbicide is not toxic to the rat, LD_{50} 1,028 mg/kg, nor to rainbow trout as the 24 hr TL_m is 35,000 ppm (Herbicide Handbook, 1970).

The metabolism of dicamba has been investigated in wheat and bluegrass, and the major degradation product is 5-hydroxy dicamba which then is conjugated (Broadhurst et al., 1966). Further, transformations in these two plant species include conjugation of dicamba and O-demethylation to give 3,6-dichlorosalicylic acid. Metabolism studies of dicamba with ring-labeled ^{14}C dicamba in rats demonstrate that this herbicide is rapidly excreted in the urine with approximately 20% of the urinary metabolites in the form of glucuronic acid conjugates (Tye and Engel, 1967). Feeding studies with dicamba in rats reveal that most residues were in the aqueous portion of the body burden and not in fatty tissues, indicating this herbicide is not stored (Tye and Engel, 1967).

The picture that emerges from examination of dicamba in the model ecosystem for the organisms as seen in Table 24 is that none of the organisms contains residues of identifiable metabolites. Only the crab contains 0.743 ppm of an unidentified conjugate, while the rest of the organisms have small amounts of extractable radioactivity and somewhat larger amounts of unextractable radioactivity. Clearly, dicamba or its metabolites do not accumulate in the organisms of this model ecosystem.

Table 22

Concentrations (ppm) of Bentazon® and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Clam	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
A	0.77	--	--	0.622	--	--	--	--	--
B	0.63	--	--	1.266	--	--	--	--	--
Bentazon®	0.52	--	--	0.510	--	--	--	--	--
I [b]	0.00	--	--	0.327	--	--	--	--	--
Extractable ^{14}C		0.109	0.032	2.72	0.182	0.092	0.012	0.146	0.084
Unextractable ^{14}C		0.759	0.021	3.08	0.407	0.168	0.036	0.716	0.378
Grand Total ^{14}C		0.868	0.054	5.80	0.98	0.26	0.048	0.86	0.462

[a] Silica Gel GF-254, benzene-ethanol, 60:40 by volume
[b] Roman numerals - unknown spots
A N-isopropyl anthranilamide
B anthranilic acid

Table 23

Concentrations (ppm) of Bentazon® and metabolites in water in a model ecosystem

Compound	R_f [a/]	Unhydrolyzed Water	Hydrolyzed Water
A	0.77	0.000691	0.0207
B	0.63	--	--
Bentazon®	0.52	0.000281	0.0502
I [b/]	0.00	0.000028	0.00303
Extractable ^{14}C		0.001	0.074
Unextractable ^{14}C		0.114	0.44
Grand Total ^{14}C		0.116	0.118

a/ Silica Gel GF-254, benzene-ethanol, 60:40 by volume
b/ Roman numerals - unknown spots
A N-isopropyl anthranilamide
B anthranilic acid

The water portion of this model ecosystem (Table 25) contains small amounts of unconjugated dicamba, 0.000289 ppm, and about 1,800x that amount in the hydrolyzed water, 0.162 ppm. The dicamba isolated after hydrolysis was a conjugate which was released through the acid treatment. Also there were small amounts of 5-hydroxy dicamba, 0.0185 ppm, released on treatment of the water with acid. The tendency for this herbicide to become conjugated in the water portion of this ecosystem is exemplified by the comparative figures for unextractable/extractable ^{14}C. For the unhydrolyzed water, >99% was in the form of unextractable radioactivity, while in the hydrolyzed water about 99% became extractable after acid hydrolysis. In the hydrolyzed extract 89% of the radioactivity was dicamba.

2,4-dichlorophenoxyacetic acid

The herbicidal properties of 2,4-dichlorophenoxyacetic acid (2,4-D and its esters) have been known for over 30 years. In view of the lengthy use of this herbicide and the availability of an excellent review of this class of herbicidal chemicals (Loos, 1969), few comments will be made about their mode of action. In general, metabolism and degradation studies that have been carried out in plants indicate three generalized metabolism pathways, namely, ring hydroxylation, side chain degradation and conjugation of the acid or phenolic moieties (Loos, 1969). Principal hydroxylated metabolites found in plants of 2,4-D are 2,3-dichloro-4-hydroxyphenoxyacetic acid and 2,5-dichloro-4-hydroxyphenoxyacetic acid which result from a chlorine shift during hydroxylation. The side chain metabolism has been demonstrated through the use of ^{14}C labeled 2,4-D and trapping of the $^{14}CO_2$ produced by oxidation of the side chain. Finally, conjugates of the ring hydroxylated metabolites and intact 2,4-D with glucose appear to be an important mode of detoxication of this herbicide by plants (Loos, 1969). In addition to the characterized metabolites, numerous unidentified metabolites from plants have been observed and corroborate the observation from the present model ecosystem work that this chemical can undergo substantial degradation.

The degradation of 2,4-D in the soil by microorganisms is optimal in warm, moist soil. Autoclaving of the soil destroys the bacteria and reduces the rate of degradation of 2,4-D. Primary degradation routes of the phenoxyacetic acids appear to go in two stages, namely, degradation to the phenol and then degradation of the phenol to carbon dioxide and water (Loos, 1969).

With regards to the environmental accumulation of 2,4-D by fish in an aquatic food web, a recent study (Schultz, 1973) has provided insight into the uptake of this herbicide by fish. In general, the three species of fish exposed to this herbicide did not accumulate it over the concentration in the water. As would be expected, fish exposed to the herbicide in water held at pH 9 contained less residues of 2,4-D than those exposed at pH 6. Further, less than 10% of the radioactivity accumulated by the fish was parent material and the major metabolite

Table 24

Concentrations (ppm) of dicamba and metabolites in organisms in a model ecosystem

Compound	R_f [a/]	Algae	Clam	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
dicamba	0.86	--	--	--	--	--	--	--	--
A	0.38	--	--	--	--	--	--	--	--
B	0.04	--	--	0.743	--	--	--	--	--
Extractable ^{14}C		0.228	0.0128	0.743	0.000	0.325	0.00665	0.0736	0.0720
Unextractable ^{14}C		1.390	0.0144	0.374	0.167	0.593	0.0122	0.281	0.252
Grand Total ^{14}C		1.618	0.0272	1.117	0.167	0.918	0.0188	0.355	0.324

[a/] Whatman No. 1 filter paper, benzene-acetic acid, 2:1 by volume
A 3,6-dichloro-5-hydroxy-2-methoxy benzoic acid
B Conjugated metabolite

Table 25

Concentrations (ppm) of dicamba and metabolites in water in a model ecosystem

Compound	R_f [a/]	Unhydrolyzed Water	Hydrolyzed Water
dicamba	0.86	0.000289	0.162
A	0.38	--	0.0185
B	0.04	0.0000114	0.000181
Extractable ^{14}C		0.000300	0.181
Unextractable ^{14}C		0.163	0.0022
Grand Total ^{14}C		0.163	0.183

a/ Whatman filter paper No. 1, benzene-acetic acid, 2:1 by volume
A 3,6-dichloro-5-hydroxy-2-methoxy benzoic acid
B Conjugated metabolite

was the glucuronic acid conjugate of 2,4-D. The small amounts of 2,4-D found in the fish demonstrate that the fish can metabolize this herbicide.

The model ecosystem experiment confirmed the earlier work regarding the propensity for 2,4-D to undergo substantial degradation and not accumulate in aquatic organisms. For example in Table 26 for the organisms, there were no residues of 2,4-D and seven unidentified metabolites. The substantial numbers of unidentified metabolites are disturbing as six metabolites, including 2,4-D, were co-chromatographed with the extracts from these organisms. The compounds chromatographed were 2,4-D, 2,3-dichloro-4-hydroxyphenoxyacetic acid, 2,4-dichloro-5-hydroxyphenoxyacetic acid, 2,5-dichloro-4-hydroxyphenoxyacetic acid, 2,4-dichlorophenol, 3,5-dichlorocatechol, 2,3-dichlorohydroquinone and 2,3-dichlororesorcinol.

The water portion of the model ecosystem experiment (Table 27) had numerous spots which did not correspond to any of the chromatographed metabolites. Interestingly, the water primarily contained metabolites which had R_f values of 0.58 or less, while the snail, algae and Elodea contained metabolites and/or degradation products with higher R_f values. This is expected as polar products remain in the water and less polar materials partition into the organisms. Clearly, 2,4-D does not accumulate in any of the organisms of this model ecosystem and appears to be degraded into water soluble compounds.

Pyrazon

Pyrazon is a herbicide used for the control of annual broadleaf weeds in sugar beets and red beets. The usual modes of application are as a preemergence, broadcast or early postemergence as a banded treatment at 2-4 lb/A. This herbicide is relatively nontoxic to mammals as the oral LD_{50} to the rat is 3,000 mg/kg (Anon. 1973). It does not leach readily through clay, clay loam or sandy clay and loam soils and has a soil persistence time of about 1-2 months (Frank, 1972). The mode of action in the susceptible plant, lambsquarters, is inhibition of the Hill Reaction which is important in photosynthesis. However, in vivo comparison of the metabolic rates of sugar beets, which are nonsusceptible, and lambsquarters, which are susceptible, shows that pyrazon accumulates in the stems and leaves in the susceptible species, while in the tolerant sugar beets the pyrazon is rapidly degraded to nonphytotoxic species. Hence, the selectivity in vivo in the comparison of sugar beets and lambsquarters lies in the greater ability of the sugar beets to degrade pyrazon (Frank, 1972).

The metabolism of pyrazon in plants and soil has been examined. In sugar beets the herbicide was degraded to three primary metabolites, two of which were positively identified. The two identified were the conjugate with the free amino group with glucose to form N-glucosyl pyrazon and desphenyl pyrazon. In the soil the only metabolite identified was the desphenylated pyrazon (Stephensen and Ries, 1969).

Table 26

Concentrations (ppm) of 2,4-D and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Elodea	Fish	Snail
I [b]	0.97	0.282	0.178	--	0.285
II	0.89	1.0295	0.456	--	--
III	0.80	0.477	0.447	--	0.301
VI	0.65	0.377	--	--	--
V	0.58	0.295	--	0.0431	--
X	0.10	1.675	0.768	--	--
XII	0.00	1.362	0.873	0.00226	0.171
Extractable ^{14}C		5.498	2.722	0.0454	0.757
Unextractable ^{14}C		17.625	7.755	0.211	6.421
Grand Total ^{14}C		23.123	10.477	0.256	7.178

[a] Silica Gel GF-254, benzene-dioxane-acetic acid, 90:25:4 by volume
[b] Roman numerals - unknown spots

Table 27

Concentrations (ppm) of 2,4-D and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
V [b]	0.58	0.000029	0.0000351
VI	0.63	0.0000914	0.00260
VII	0.56	0.0000658	0.00205
VIII	0.49	--	0.00226
IX	0.39	--	0.000417
X	0.10	--	0.000474
XI	0.067	--	0.000271
XII	0.00	0.00000496	0.000180
Extractable ^{14}C		0.000191	0.000829
Unextractable ^{14}C		0.0128	0.0120
Grand Total ^{14}C		0.0130	0.0128

[a] Silica Gel GF-254, benzene-dioxane-acetic acid, 90:25:4 by volume
[b] Roman numerals - unknown spots

The data for the distribution of metabolites and degradation products in the organisms of pyrazon are in Table 28. Again, as in the case of the 2-chloroacetanilides, no identifiable compounds with the exception of the crab, 0.476 ppm, had residues of either pyrazon or degradation products. Further, very little of the radioactivity (extractable and unextractable) was isolated from any of the organisms (0.0573 ppm for fish to 0.629 ppm for crab), which may be explained by the relatively high water solubility of pyrazon, 300 ppm (Anon. 1970).

The water portion of this ecosystem (Table 29) contains five unidentified metabolites not found in the organisms, including pyrazon at 0.212 ppm and the desphenyl pyrazon at 0.0714 ppb. Clearly, pyrazon shows a similar pattern to the 2-chloroacetanilides as it is not accumulated by the organisms of the model ecosystem, but degrades to polar, water soluble metabolites.

Trifluralin®

Trifluralin® , or treflan, is one of many dinitroaniline herbicides which include Cobex®, Nitralin® and Benefin®. These herbicides have found extensive use in soybeans to control common annual grasses, pigweed and lambsquarters and are usually applied as either a preplant or preemergence application. Trifluralin® is best suited for soils with 3% organic matter or less (Wax, 1973). Extensive toxicological data obtained on Trifluralin® indicate a low order of acute toxicity, LD_{50} to rats of >10 g/kg, LC_{50} of an emulsifiable concentrate to bluegills, fathead minnows and goldfish of 0.58 ppm, 0.94 ppm and 0.59 ppm, respectively (Parka and Worth, 1965).

The metabolism of Trifluralin® in plants, animals and soil as well as photodecomposition has been investigated. In addition, the anaerobic degradation of this herbicide has been examined. The pathways for degradation of this herbicide have been the subject of an excellent review (Probst and Tepe, 1969) and, therefore, will only be discussed briefly. Degradation of Trifluralin® in the soil under aerobic conditions leads to numerous products, including the mono- and didealkylated derivatives of Trifluralin®, as well as mono- and didealkylated Trifluralin® with one of the 2,6-nitro groups reduced to an amine. A final metabolite isolated from the aerobic system is the conjugated α,α,α-trifluorotoluene-3,4,5-triamine.

The experiment with Trifluralin® was carried out twice employing different modes of application. The normal-use pattern of Trifluralin® is a soil treatment, so the analogous treatment in the model ecosystem would be treatment of the sand at evenly spaced intervals (2.5 cm apart) with 5 mg which corresponds to about 1 lb/A. Since sorghum is susceptible to Trifluralin®, a common variety of soybeans was grown in place to establish the viability of the sand for plant growth. While the Trifluralin® in this case was a sand treatment, no caterpillars were added to act as the first stage of the food chain as well as a dispersing agent. The sand treatment was then compared to the normal

Table 28

Concentrations (ppm) of pyrazon and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Clam	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
pyrazon	0.63-0.69	--	--	0.476	--	--	--	--	--
A	0.47-0.51	--	--	--	--	--	--	--	--
I [b]	0.40-0.43	--	--	--	--	--	--	--	--
II	0.23	--	--	--	--	--	--	--	--
III	0.16	--	--	--	--	--	--	--	--
IV	0.10	--	--	--	--	--	--	--	--
V	0.00	--	--	0.0233	--	--	--	--	--
Extractable ^{14}C		0.0758	0.0498	0.499	0.0536	0.105	0.0336	0.175	0.127
Unextractable ^{14}C		0.131	0.0180	0.130	0.0455	0.0552	0.0237	0.148	0.0592
Grand Total ^{14}C		0.207	0.0678	0.629	0.0991	0.160	0.0573	0.323	0.186

[a] Silica Gel GF-254, benzene-ethanol, 60:40 by volume
[b] Roman numerals - unknown spot
A 5-amino-4-chloro-3(2H)pyridazinone

Table 29

Concentrations (ppm) of pyrazon and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
pyrazon	0.63-0.69	0.0112	0.00998
A	0.47-0.51	--	0.0000714
I [b]	0.40-0.43	--	0.0000430
II	0.23	--	0.0000260
III	0.16	--	0.0000471
IV	0.10	--	0.0000764
V	0.00	0.0000300	0.000106
Extractable ^{14}C		0.0112	0.0103
Unextractable ^{14}C		0.0203	0.0105
Grand Total ^{14}C		0.0315	0.0208

[a] Silica Gel GF-254, benzene-ethanol, 60:40 by volume
[b] Roman numerals - unknown spots
A 5-amino-4-chloro-3(2H)pyridazinone

sorghum treatment which is the standard mode of application of pesticides in the model ecosystem. The discussion of Trifluralin® will then engender a comparison of the two methods of application and its effect on the persistence and degradation pattern of this herbicide.

In Tables 30 and 32 are the data for the distribution of the metabolites in the organisms of the sand- and sorghum-treated Trifluralin® ecosystems. Several interesting differences are related to the two treatments as the snail and fish contain more Trifluralin® in the sand-treated system than in the sorghum-treated system. This is shown by the data which indicates that the snail and fish contained about 5.4x and 3.0x more herbicide in the sand experiment. Another striking difference is the lack of algae in the sorghum treatment and the existence of algae in the sand-treated ecosystem. The caterpillar, which is the dispersing agent and the first member of the food chain, apparently spread residues of Trifluralin® more efficiently into the water which were phytotoxic and, therefore, inhibited the growth of the algae in the sorghum treatment.

The data for the water portion of the model ecosystem (Tables 31 and 32) support the role of the caterpillar in spreading the Trifluralin® and metabolites in the system as the total radioactivity in the water at the end of the experiment was about 6.4x greater in the sorghum-treated ecosystem as compared with the sand-treated system. Apparently, the Trifluralin® is adsorbed on the sand and therefore does not dissolve in the water. In contrast to the approximately 6-fold difference in total radioactivity in the water of the sorghum-treated system, the amount of Trifluralin® in the water is only 1.5x greater in the sorghum treatment than in the sand treatment. Finally, the concentration of Trifluralin® by the organisms appears to be affected by the type of treatment as the values for accumulation of Trifluralin® over the concentration in the water by the fish and snail in the sand treatment is 4,200x and 153,000x, respectively. In the sorghum treatment the values for the fish and snail are 930x and 17,700x, respectively. The caterpillar which degrades Trifluralin® in the sorghum treatment, as well as the opportunity for Trifluralin® to undergo photodecomposition on the sorghum leaves before consumption by the caterpillar, have a substantial effect on the persistence of this herbicide as demonstrated by the accumulation factors for the snail and fish. The accumulation factors of Trifluralin^{R} for the fish and snail are in the same order of magnitude as that obtained for methoxychlor which was accumulated ~1,500x by the fish and about 123,000x by the snail (Metcalf et al., 1973). The snail is incapable of degrading even the most biodegradable DDT analogue, methoxychlor, as well as the herbicide, Trifluralin®.

Table 30

Concentrations (ppm) of Trifluralin® and metabolites in organisms in a model ecosystem after sorghum treatment

Compound	R_f[a]	Daphnia	Fish	Mosquito	Snail
Trifluralin®	0.74	--	0.261	--	5.046
I[b]	0.51	--	--	--	--
A	0.39	--	--	--	0.337
C	0.32	--	--	--	--
II	0.24	--	--	--	0.0399
III	0.20	--	--	--	0.216
IV	0.17	--	--	--	--
E	0.13	--	--	--	--
V	0.11	--	--	--	--
VI	0.07	--	--	--	0.228
VII	0.04	--	--	--	--
VIII	0.00	--	0.506	--	0.796
Extractable ^{14}C		0.445	0.767	0.238	6.535
Unextractable ^{14}C		1.017	1.011	0.520	6.648
Grand Total ^{14}C		1.462	1.777	0.758	13.183

Table 30 (con't.)

a/
b/ Silica Gel GF-254, hexane-acetone-MeOH, 90:10:2 by volume
Roman numerals - unknown spots
A α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine
C 2,6-dinitro-4-trifluoroaniline
E 2-ethyl-5-trifluoromethyl-7-nitrobenzimidazole

Table 31

Concentrations (ppm) of Trifluralin® and metabolites in water in a model ecosystem after sorghum treatment

Compound	R_f [a/]	Unhydrolyzed Water	Hydrolyzed Water
Trifluralin®	0.74	0.000282	--
I	0.51	0.000066	--
A	0.39	0.000087	--
C	0.32	0.000374	--
II	0.24	0.000322	--
III	0.20	0.000139	--
IV	0.17	0.000315	0.000199
E	0.13	0.000475	0.000328
V	0.11	0.000415	0.000271
VI	0.07	0.000928	0.000486
VII	0.04	0.00123	0.000800
VIII	0.00	0.00526	0.0116
Extractable ^{14}C		0.00989	0.0137
Unextractable ^{14}C		0.0290	0.0253
Grand Total ^{14}C		0.0388	0.0290

a/ Silica Gel GF-254, hexane-acetone-MeOH, 90:10:2 by volume
b/ Roman numerals - unknown spots
A α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine
C 2,6-dinitro-4-trifluoroaniline
E 2-ethyl-5-trifluoromethyl-7-nitrobenzimidazole

Table 32

Concentrations (ppm) of Trifluralin® and metabolites in organisms in a model ecosystem after sand treatment

Compound	R_f [a]	Algae	Daphnia	Fish	Mosquito	Snail
Trifluralin®	0.74	--	--	0.775	--	27.085
I [b]	0.61	--	--	0.167	--	0.667
A	0.56	--	--	0.179	--	--
B	0.36	--	--	--	--	0.323
D	0.22	--	--	0.04	--	--
E	0.09	--	--	0.052	--	--
V	0.00	--	--	0.138	--	0.766
Extractable ^{14}C		0.350	0.317	1.323	0.208	28.870
Unextractable ^{14}C		0.475	0.311	0.129	0.168	0.183
Grand Total ^{14}C		0.825	0.628	1.452	0.376	29.053

[a] Silica Gel GF-254, hexane-acetone-MeOH, 90:10:2 by volume
[b] Roman numerals - unknown spots
A α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine
B N,N-dipropyl-3-nitro-5-trifluoromethyl-o-phenylenediamine
D 2-ethyl-5-trifluoromethyl-7-nitro-1-propylbenimidazole
E 2-ethyl-5-trifluoromethyl-7-nitrobenzimidazole

Table 33

Concentrations (ppm) of Trifluralin® and metabolites in water in a model ecosystem after sand treatment

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
Trifluralin®	0.74	0.000184	--
I [b]	0.61	0.0000343	--
A	0.56	--	0.0000104
II	0.48	--	--
B	0.36	--	--
C	0.27	0.000140	--
D	0.22	0.0000917	--
III	0.14	0.000111	0.000017
E	0.09	0.000414	0.0000737
IV	0.05	0.000597	0.000299
V	0.00	0.00144	0.000687
Extractable ^{14}C		0.00301	0.00109
Unextractable ^{14}C		0.00383	0.00274
Grand Total ^{14}C		0.00684	0.00383

[a] Silica Gel GF-254, hexane-acetone-MeOH, 90:10:2 by volume
[b] Roman numerals - unknown spots
A α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine
B N,N-dipropyl-3-nitro-5-trifluoromethyl-o-phenylenediamine
D 2-ethyl-5-trifluoromethyl-7-nitro-1-propylbenimidazole
E 2-ethyl-5-trifluoromethyl-7-nitrobenzimidazole

SECTION V

EXAMINATION OF A MITICIDE, SELECT PLASTICIZERS, A FUNGICIDE AND A BACTERIOSTAT

The final segment of this report of the fate of select pesticides in the aquatic environment deals with a miticide, two types of plasticizers, a fungicide and a bacteriostat. The miticide was chosen as little environmental information is known about acaricides in general and further, this is a new class of miticide which has not yet found generalized use. Therefore, it would be of interest to examine the persistence and uptake of this pesticide by the organisms of the model ecosystem before it is used in large quantities in the environment.

Two types of plasticizers were examined in the model ecosystem because they have been demonstrated to be pollutants of fish, birds and many other forms of wildlife. In contrast to the previously discussed pesticides, these compounds were not purposefully applied to control a pest, but have become pollutants unintentionally as the result of either industrial discharge during production or from seepage into the environment during their intended use. The high lipid solubility, inertness to chemical and biological degradation, particularly for the higher chlorinated PCB's, and coupled with their multibillion pound production clearly explains the worldwide occurrence of these materials in the environment.

The examination of captan in the model ecosystem was important for two reasons. First, the use of fungicides containing mercury is now generally considered to be both environmentally unsafe as well as hazardous to human health. The mercury fungicides are quite toxic to humans and can cause severe poisoning when ingested. Some adults and children in New Mexico and Iran mistakenly utilized grain treated with mercury fungicides for feed for swine and for making bread and, as a result, they suffered from acute mercury posioning. Secondly, captan has been used for about 20 years without apparent environmental problems related to persistence and food web magnification. In order to validate the use of the model ecosystem as a useful tool for prediction of pesticide persistence in food chain accumulation, it is necessary to examine compounds, such as captan, which have had little environmental impact after widespread use, as well as persistent compounds, such as dieldrin, DDT or aldrin. If both ends of the persistence spectrum do not agree both in the field and the model ecosystem, then this system would be of little value as a predictive tool for new pesticides.

Banomite®

Banomite® is a new class of miticidal benzoyl chloride phenylhydrazines which is being developed for the control of mites which attack citrus (Kaugers et al., 1973: Moon et al., 1972). Since these are a new class of acaricides, environmental information or metabolism data on these compounds has not been published.

The data contained in Table 34 describe the distribution of Banomite® and its degradation products in the organisms of the model ecosystem. Three of the organisms contain small residues of Banomite®, in particular the crab, 0.0156 ppm; Elodea, 0.041 ppm and the mosquito larvae with 0.0736 ppm. The only other metabolism or degradation product that could be identified in the organisms is the hydrolysis product of Banomite®, benzoic acid 2,4,6-trichlorohydrazide. The algae, crab, Elodea, mosquito and snail contained 0.142 ppm, 0.0364 ppm, 0.0515 ppm, 0.300 ppm and 0.306 ppm, respectively, of this metabolite. In addition to the two identified compounds, there were eight other unidentified metabolites. This acaricide is labile and undergoes degradation to the numerous metabolites isolated from the organisms. The snail and fish contain considerable amounts of unidentified Metabolite II with 10.69 ppm and 1.62 ppm, respectively.

Examination of the data for the water (Table 35) for Banomite® shows a similar distribution of Banomite® and degradation products. There were small amounts of the two characterized compounds, namely, Banomite® at 18.62 ppt and benzoic acid 2,4,6-trichlorophenylhydrazide at 294 ppt. The value for the water concentration of Banomite®, when divided into those organisms which contained this miticide, reveal that the crab, Elodea and mosquito accumulated Banomite® from the water 840x, 2,200x and 4,000x, respectively. The other degradation product, or metabolite which was found in the organisms, benzoic acid 2,4,6-trichlorophenylhydrazide, was accumulated from the water by the algae, crab, Elodea, mosquito and snail 500x, 125x, 175x, 1,000x and 1,000x, respectively. However, the unidentified Metabolite II was accumulated from the water by the fish 3,000x and the snail ∿19,000x, and therefore its structure should be investigated further to determine if this metabolite has any physiological effect at this level.

Di-n-octyl phthalate (DOP)

The concern for environmental quality has stimulated interest in the disposition of substances which interfere with residue analysis, such as the polychlorinated biphenyls (PCB's) and the phthalate ester plasticizers. The latter are produced in enormous quantities, for example, some 4.5×10^7 lbs in 1972 (Anon. 1972). The phthalate esters, which as pollutants occur in fish taken from streams and rivers in the United States (Mayer et al., 1972), appear to have a low order of acute toxicity to aquatic organisms (Sanders et al., 1973); but, for instance, di-2-ethylhexyl phthalate, the largest produced phthalate plasticizer, accumulates in snails, mosquito larvae and mosquito fish in a model ecosystem experiment (Metcalf et al., 1973). Therefore, to establish the relationship between plasticizer chemical structure and environmental persistence, di-n-octyl phthalate was examined in the model ecosystem.

Previous model ecosystem studies with di-2-ethylhexyl phthalate (DEHP) demonstrated that this phthalate ester was degraded to mono 2-ethylhexyl phthalate and phthalic acid (Metcalf et al., 1973). Only

Table 34

Concentrations (ppm) of Banomite® and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Clam	Crab	Daphnia	Elodea	Fish	Mosquito	Snail
Banomite®	0.75	--	--	0.0156	--	0.0410	--	0.0736	--
I [b]	0.61	--	--	--	--	0.0928	--	0.266	0.565
II	0.53	0.963	2.044	0.0670	0.686	1.048	1.624	0.453	10.685
III	0.35	0.181	--	0.0568	--	0.0662	0.378	0.265	1.160
A	0.27	0.142	--	0.0364	--	0.0515	--	0.300	0.306
IV	0.21	0.202	--	--	--	--	--	--	--
V	0.14	0.269	0.227	0.0406	--	0.185	0.0943	0.324	2.549
VI	0.07	--	--	--	--	--	0.0452	0.286	0.938
VII	0.03	0.514	--	0.140	--	0.059	--	0.533	0.478
VIII	0.00	0.923	0.0703	1.00850	0.255	0.328	0.180	1.652	0.872
Extractable ^{14}C		3.191	2.342	1.366	0.941	1.874	2.323	4.156	17.542
Unextractable ^{14}C		6.602	0.136	1.0878	0.877	1.445	0.451	2.137	1.777
Grand Total ^{14}C		9.793	2.478	2.454	1.818	3.319	2.774	6.293	19.319

[a] Silica Gel GF-254, n-hexane-ethyl acetate, 80:20 by volume
[b] Roman numerals - unknown spots
A benzoic acid 2,4,6-trichlorophenyl hydrazide

Table 35

Concentrations (ppm) of Banomite® and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
Banomite®	0.75	0.00000892	0.0000097
I [b]	0.61	0.0000602	0.0000328
II	0.53	0.000444	0.0000948
III	0.35	0.000452	0.000688
A	0.27	0.000141	0.000153
IV	0.21	0.000110	0.000184
V	0.14	0.000693	0.00157
VI	0.07	0.00180	0.000682
VII	0.03	0.000662	0.00362
VIII	0.00	0.00176	0.0093
Extractable ^{14}C		0.00612	0.0164
Unextractable ^{14}C		0.0243	0.00599
Grand Total ^{14}C		0.0304	0.0224

[a] Silica Gel GF-254, n-hexane-ethyl acetate, 80:20 by volume
[b] Roman numerals - unknown spots
A benzoic acid-2,4,6-trichlorophenyl hydrazide

the mosquito larvae, snail and mosquito fish accumulated from the water DEHP 100,000x, 21,000x and 130x, respectively.

The data for the distribution of DOP in the organisms of the model ecosystem are collected in Table 36. The algae contained the most DOP at 1.80 ppm, the snail with the next highest at 0.85 ppm, the fish and mosquito at 0.59 ppm and Daphnia at 0.10 ppm. In addition to DOP there were about six unidentified metabolites, but no mono octyl phthalate was isolated from any of the organisms. In all cases, except the fish, most of the radioactivity averaged about 75% unextractable, whereas the fish had only about 22% unextractable. Perhaps the low titer of liver microsomal enzymes in Gambusia affinis (Krieger and Lee, 1973) accounts for the inability of the fish to convert DOP to polar unextractable products.

The water portion of this model ecosystem experiment as indicated in Table 37 contained small amounts of DOP, 6.3 ppt, no mono octyl phthalate and small amounts of phthalic acid, 0.782-1.82 ppb. Using the values obtained for the amounts of DOP in the water and organisms, concentration factors can be calculated for algae 28,500x, Daphnia 2,600x, fish and mosquito larvae 9,400x and 13,600x for the snail. Previous ecosystem evaluation of the branched DEHP indicated that this plasticizer was accumulated from the water by the snail 21,000x, the mosquito fish 130x and the mosquito larvae 100,000x. With only two esters examined in this model ecosystem, it is difficult to account for the differences in the uptake of these structurally related plasticizers. It is obvious that despite the susceptibility of these two plasticizers to undergo substantial degradation, their high lipid solubility accounts for their uptake and storage in the organisms of this model ecosystem (Mayer et al., 1972).

Polychlorinated Biphenyls

The ubiquitous occurrence of polychlorinated biphenyls (PCB's) in the environment has been well reviewed (Peakall, 1972) and, therefore, a few brief comments will be made about their chemical and environmental properties. The industrial PCB's are a complex mixture of chlorinated biphenyls which have a multitude of uses including heat-transfer fluids, plasticizers and extenders for pesticides. The inert chemical properties of these compounds make them excellent in their numerous applications, but, because of their environmental stability and high lipid solubility, they have been found in the lipoidal tissues of numerous animals, principally in fish (Henderson, 1971) and birds (Risebrough, 1969). The primary production of polychlorinated biphenyls in the United States is by the Monsanto Company under the trade name Aroclor® 1254, 1242, 1221, etc., where the first two digits identify it as a derivative of biphenyl which has 12 carbons and the last two digits relate to the average percent chlorine, i.e., 1254 has 54% chlorine.

Table 36

Concentrations (ppm) of di-n-octyl phthalate and metabolites in organisms of a model ecosystem

Compound	R_f [a]	Algae	Daphnia	Fish	Mosquito	Snail
DOP	0.92	1.7963	0.1645	0.5920	0.5925	0.8543
I [b]	0.73	0.6709	--	--	0.1748	0.0545
II	0.53	0.3356	0.1425	0.0357	0.4855	0.1643
III	0.47	0.3797	0.1722	0.0374	0.1641	0.1477
IV	0.35	0.0808	--	--	0.0906	--
VI	0.25	--	--	--	--	0.0569
VII	0.00	7.3654	1.2001	0.2649	0.3314	0.2882
Extractable ^{14}C		10.6348	1.6793	0.9300	1.8389	1.5659
Unextractable ^{14}C		43.2011	7.4703	0.3974	6.7225	2.9077
Grand Total ^{14}C		53.8359	9.1488	1.3273	8.5614	4.4736

[a] Silica Gel GF-254, benzene-acetone-petroleum ether-acetic acid, 50:5:25:1 by volume
[b] Roman numerals, unknown spots

Table 37

Concentrations (ppm) of di-n-octyl phthalate and metabolites in organisms of a model ecosystem

Compound	R_f[a]	Unhydrolyzed Water	Hydrolyzed Water
DOP	0.92	0.000063	--
I[b]	0.73	0.000020	--
II	0.53	0.00001	--
III	0.47	0.000041	0.000098
IV	0.35	--	0.000031
V	0.30	--	0.000182
VI	0.25	--	0.000320
phthalic acid	0.07	0.000197	0.001103
VII	0.00	0.000045	0.000783
Extractable ^{14}C		0.000376	0.002515
Unextractable ^{14}C		0.005993	0.003478
Grand Total ^{14}C		0.006390	0.005993

[a] Silica Gel GF-254, benzene-acetone-petroleum ether-acetic acid, 50:5:25:1 by volume

[b] Roman numerals - unknown spots

The initial studies with the PCB's and animals were carried out with the complex mixtures which make analysis of the metabolites and change in the constitution of the PCB mixture very difficult. However, with the recent availability of pure ^{14}C isomers of three of the PCB's, more precise studies on the uptake and metabolism of PCB's can be undertaken. The three labeled PCB's currently available from the Mallinckrodt Chemical Company are 2,5,2'-trichlorobiphenyl, 2,5,2',5'-tetrachlorobiphenyl and 2,4,5,2',5'-pentachlorobiphenyl. Through the cooperation of Professor Robert L. Metcalf, University of Illinois, it was possible that these compounds could be obtained for model ecosystem studies in his laboratory.

The data in Table 38 contain the distribution in both the water and organisms for the three pure isomer ^{14}C PCB's. An interesting aspect of the data is the gradual increase in concentration of the three compounds as the chlorine number is increased from three to five. For example, the fish contains 1.28 ppm trichlorobiphenyl, 14.24 ppm tetrachlorobiphenyl and 119.71 ppm pentachlorobiphenyl. For the snail the increased accumulation of the biphenyls is similar to the fish, but the levels are higher as 18.97 ppm trichlorobiphenyl, 47.33 ppm tetrachlorobiphenyl and 587.35 ppm for pentachlorobiphenyl were isolated from this organism.

Another significant aspect of the data is the gradual decrease in percent unextractable radioactivity in the fish as the number of chlorine substituents is increased from three to five. The percentage values for the unextractable radioactivity are 15% for the trichlorobiphenyl, 2.44% for the tetrachlorobiphenyl and 1.10% for the pentachlorobiphenyl, which indicates the relative susceptibility of these three compounds to undergo metabolism by the fish.

One last comment regards the relative accumulation from the water of these PCB's by the snail and fish. The fish accumulated the 3-, 4- and 5-chlorinated biphenyls 6,400x, 11,863x and 12,153x, respectively, the concentration in the water. The snail showed a greater differential between the numbers of chlorine substituents and accumulation values as the 3-, 4- and 5-chlorinated biphenyls accumulated 5,795x, 39,439x and 59,629x, respectively, the water concentration. This differential between accumulation factors for the snail as compared to the fish may reflect the greater metabolic capacity of the fish to transform these lipid soluble compounds to water soluble compounds after they are taken up from their environment.

Captan

This nonmercury fungicide is widely employed as an effective agent for the control of fungus in vegetables, fruits and ornamentals. In addition, it is utilized as an effective seed treatment. The safety of this fungicide to rats is demonstrated by its oral LD_{50} of >15,000 mg/kg and an intravenous LD_{50} of 50-100 mg/kg (Metcalf, 1971). Feeding studies conducted with captan for a 2-year period at 10,000 ppm with

Table 38

Distribution of chlorinated biphenyls and their degradation products in the model ecosystem

chlorinated biphenyl equivalents - ppm

	H_2O	Oedogonium (alga)	Physa (snail)	Culex (mosquito)	Gambusia (fish)
I. 2,5,2'-trichlorobiphenyl total ^{14}C	0.03845	23.2155	31.2015	2.7030	3.2055
Unknown I (R_f 0.66*)	0.00015	15.9575	18.9720	1.1995	0.2085
trichlorobiphenyl (R_f 0.56)	0.00020	1.4630	1.1590	0.1630	1.2800
Unknown II (R_f 0.23)	0.00005	0.0520	0.6480	--	0.1595
Unknown III (R_f 0.10)	--	--	0.9735	--	--
Unknown IV (R_f 0.06)	0.00055	--	0.5460	--	--
Unknown V (R_f 0.04)	0.00040	--	0.2205	--	--
Unknown VI (R_f 0.03)	0.00040	0.0685	0.4410	--	--
Polar (R_f 0.0)	0.02265	0.5185	3.9315	0.4795	0.9985
Unextractable	0.01405	5.1560	4.3100	0.8610	0.5590

Table 38 (con't.)

		H_2O	Oedogonium (alga)	Physa (snail)	Culex (mosquito)	Gambusia (fish)
II.	2,5,2',5'-tetrachlorobiphenyl total ^{14}C	0.02065	23.6845	53.7465	14.5335	15.5685
	tetrachlorobiphenyl (R_f 0.48*)	0.00120	21.5975	47.3275	12.6745	14.2360
	Unknown I (R_f 0.23)	0.00005	0.3220	0.7560	0.1070	0.0890
	Unknown II (R_f 0.04)	0.00155	0.1030	0.4360	--	--
	Polar (R_f 0.0)	0.01225	0.3275	3.9850	0.9670	0.8545
	Unextractable	0.00560	1.3345	1.2420	0.7850	0.3900
III.	2,5,2',4',5'-pentachlorobiphenyl total ^{14}C	0.04340	62.4660	633.0165	181.4565	127.6945
	pentachlorobiphenyl (R_f 0.55*)	0.00985	53.8440	587.3545	170.8480	119.7060
	Unknown I (R_f 0.46)	--	0.6850	8.6210	2.4070	2.5380
	Unknown II (R_f 0.39)	0.00020	0.5080	2.2490	1.3195	0.5810
	Unknown III (R_f 0.21)	0.00015	0.1425	1.9365	1.0520	0.3285
	Unknown IV (R_f 0.04)	0.00030	--	0.5000	--	--
	Unknown V (R_f 0.02)	0.00385	0.2570	7.4965	--	0.7450

Table 38 (con't.)

	H_2O	Oedogonium (alga)	Physa (snail)	Culex (mosquito)	Gambusia (fish)
Polar (R_f 0.0)	0.02055	1.6265	16.5550	2.6745	2.3610
Unextractable	0.00850	5.4330	8.3040	3.1555	1.4350

*TLC with hexane (Skelly solve B b.p. 60-68°C)

rats showed no adverse effects. The mode of action of this compound is not clear as early work by Kittleson in 1952 suggests that the activity of this compound was related to the presence of the trichloromethyl group. Later (Rich, 1960), the fungicidal activity was ascribed to the production of thiophosgene after the displacement of the trichloromethyl group by a mercaptan group.

There appears to be some information about the environmental stability of captan. The water solubility is reported to be less than 10 ppm and undergoes hydrolysis in water of pH 7.0. In addition, the trichloromethyl sulfur moiety reacts readily with free thiol groups in biological systems (Lukens, 1969). The degradation in soil appears to proceed via hydrolysis with soil microorganisms playing a significant role (Lukens, 1969). The half-life in a moist, silt soil is about 3-4 days and much longer in an air-dried soil (Burchfield, 1959). The structures of the metabolites in soil are not completely known, although the existence of carbonyl sulfide as a product has been demonstrated (Somers et al., 1967).

The behavior of captan in this terrestrial-aquatic model ecosystem corroborates the previous data obtained from field experiments as none of the organisms after 33 days contained residues of this fungicide (Table 39). In view of the alkaline pH of the aqueous portion of the system, the captan undoubtedly under went hydrolysis as soon as it came in contact with the water. There were small amounts of unidentifiable residues in the snail, fish and algae, but no captan, which had an R_f of 0.3, was isolated from the organisms. The interesting aspect of the metabolites isolated from the snail was that they were much less polar than captan. Since the label was located on the trichloromethyl moiety, perhaps the three spots are the result of a disulfide exchange with captan and another mercaptan.

The water portion of the model ecosystem (Table 40) does not contain any traces of captan nor any of the nonpolar metabolites found in either the algae or snail. Again as demonstrated for the organisms, captan does not persist in the water as there were only metabolites which had R_f values less than 0.35. It appears that continued use of captan will not have any serious environmental impact as it does not persist in the water of this 33-day model ecosystem, nor does it accumulate in the fish which is the upper member of the food chain. The probable reason for the nonpersistence of this fungicide in this model ecosystem is the extremely labile trichloromethyl sulfur-nitrogen bond which can be split either by hydrolysis or reaction with mercaptan groups in biological systems.

Hexachlorophene

The final compound to be examined in the model ecosystem is the bacteriostat, hexachlorophene. The use of this antibacterial agent has been restricted because of the reported poisonings in France from baby powder that contained this compound. Almost nothing is known about

Table 39

Concentrations (ppm) of Captan and metabolites in organisms in a model ecosystem

Compound	R_f [a]	Algae	Daphnia	Fish	Mosquito	Snail
I [b]	0.93	0.0278	--	--	--	0.0592
II	0.85	0.0077	--	--	--	0.0795
III	0.81	--	--	--	--	0.0679
IV	0.79	0.0166	--	--	--	--
V	0.68	--	--	0.0492	--	--
VI	0.39	0.0105	--	--	--	--
VII	0.35	--	--	--	--	--
VIII	0.33	0.0142	--	--	--	--
IX	0.26	--	--	--	--	--
X	0.25	0.00608	--	--	--	--
XI	0.18	--	--	--	--	--
XII	0.14	--	--	--	--	--
XIII	0.10	0.0590	--	--	--	--
XIV	0.053	0.0159	--	0.00215	--	--
XV	0.00	0.122	--	0.000861	--	0.00940

Table 39 (con't.)

Compound	R_f [a/]	Algae	Daphnia	Fish	Mosquito	Snail
Extractable ^{14}C		0.280	0.393	0.0522	0.0462	0.216
Unextractable ^{14}C		0.967	0.338	0.0158	0.0584	0.0998
Grand Total ^{14}C		1.247	0.731	0.0680	0.105	0.316

a/ Silica Gel GF-254, petroleum ether-acetone, 4:1 by volume
b/ Roman numerals - unknown spots

Table 40

Concentrations (ppm) of Captan and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
I [b]	0.93	--	--
II	0.85	--	--
III	0.81	--	--
IV	0.79	--	--
V	0.68	--	--
VI	0.39	--	--
VII	0.35	0.00000426	--
VIII	0.33	--	--
IX	0.26	0.00000960	--
X	0.25	--	0.00000893
XI	0.18	0.00000456	--
XII	0.14	0.00000273	0.00000812
XIII	0.10	0.00000365	--
XIV	0.053	0.0000648	0.0000243
XV	0.00	0.00000761	0.0000277
Extractable ^{14}C		0.0000971	0.0000691
Unextractable ^{14}C		0.000846	0.000777
Grand Total ^{14}C		0.000943	0.000846

a/ Silica Gel GF-254, petroleum ether-acetone, 4:1 by volume
b/ Roman numerals - unknown spots

this bisphenol and its metabolic products, though studies with rats (Wit and Van Genderen, 1962) and cows (St. John and Lisk, 1972) have demonstrated that the majority of the hexachlorophene is excreted unchanged in the urine and feces when fed to these animals. However, no attempt was made to identify any of the metabolites. While some work has been carried out on the metabolism of this compound in animals, nothing is known about the environmental fate of this material except that it is thought to persist in surface waters for long periods of time without undergoing substantial degradation (Bandt and Nehring, 1962). Recently, hexachlorophene (HCP) has been detected in sewer influents in Oregon at levels of 20-31 ppb and in river water upstream from the city of Corvallis, Oregon, at 0.01-0.10 ppb. Sewer treatment of the influent removed about 60-70% of the HCP (Buhler et al., 1973). In view of the mammalian toxicity of hexachlorophene (Nakaue et al., 1973) and the dearth of environmental degradation information, it is imperative to carry out some preliminary studies on the fate of HCP in this model ecosystem.

The data for the fate of HCP in the organisms and water of this model ecosystem are contained in Tables 41 and 42. The first aspect noticed is the absence of Daphnia and mosquito larvae from the table. This indicates that these organisms did not contain sufficient radioactivity to be chromatographed. Three of the organisms, algae, 1.99 ppm; fish, 0.37 ppm; and snail, 1.31 ppm contained identifiable amounts of hexachlorophene along with several other uncharacterized metabolites. Hexachlorophene represented about 42.8% of the total radioactivity in the algae, 18.3% in the fish and 17.4% in the snail. The rest of the radioactivity in these organisms was distributed among ten uncharacterized metabolites. While there were a substantial number of metabolites in the three organisms, the unextractable radioactivity was highest for the snail, 38%, intermediate for the algae, 25% and lowest for the fish, 5.5%.

The water portion of the model ecosystem has small amounts of HCP, 0.00134 ppm, as well as numerous uncharacterized metabolites. If the figure for the hexachlorophene concentration in the water, 0.00134 ppm, is divided into the concentrations of HCP in the various organisms, concentration factors for the algae, 1,500x; fish, 278x; and snail, 970x are derived. It can be concluded that the uptake of hexachlorophene by the fish is similar to that found for parathion, which had a concentration factor of about 335x. Finally, the unextractable radioactivity in the water amounts to about 36%, which indicates that hexachlorophene is not extensively degraded to polar, unextractable metabolites either by the organisms or chemical factors, such as hydrolysis or photolysis. The inert nature of hexachlorophene is related to its polar nature resultant from the two hydroxyl groups and the highly substituted aromatic ring with chlorine and a methylene bridge. Higher chlorinated phenols such as 2,4,5-trichlorophenol and 2,3,4,6-tetrachlorophenol require about 10 weeks to undergo ring cleavage in soil (Alexander, 1972). The 2,3,4,6-tetrachlorophenol is

precisely the same arrangement of substituents of hexachlorophene, except the two position of HCP is filled by a methylene bridge instead of a halogen.

Table 41

Concentrations (ppm) of hexachlorophene and metabolites in organisms in a model ecosystem

Compound	R_f[a/]	Algae	Fish	Snail
hexachlorophene	0.89	1.994	0.371	1.309
I[b/]	0.82	0.608	1.233	--
II	0.75	--	--	--
III	0.70	--	--	--
IV	0.65	--	--	2.182
V	0.53	0.563	--	--
VI	0.23	0.0451	0.151	0.638
VII	0.14	0.259	0.0261	--
VIII	0.07	--	0.0810	--
IX	0.00	--	--	0.638
Extractable ^{14}C		3.469	1.861	4.767
Unextractable ^{14}C		1.195	0.109	2.893
Grand Total ^{14}C		4.664	1.970	7.650

a/ Silica Gel GF-254, benzene-methanol-acetic acid, 45:8:4 by volume
b/ Roman numerals - unknown spots

Table 42

Concentrations (ppm) of hexachlorophene and metabolites in water in a model ecosystem

Compound	R_f [a]	Unhydrolyzed Water	Hydrolyzed Water
hexachlorophene	0.89	0.000542	0.000798
I [b]	0.82	--	0.000444
II	0.75	0.00120	0.00130
III	0.70	--	0.00374
IV	0.65	0.00183	0.00609
V	0.53	0.000132	0.000536
VI	0.23	0.0000696	0.00384
VII	0.14	--	0.000542
VIII	0.07	--	--
IX	0.00	0.00000794	0.000238
Extractable ^{14}C		0.00378	0.01753
Unextractable ^{14}C		0.03080	0.00556
Grand Total ^{14}C		0.03458	0.02309

[a] Silica Gel GF-254, benzene-methanol-acetic acid, 45:8:4 by volume
[b] Roman numerals - unknown spots

Table 43

Accumulation factors for fish and snail for compounds examined in the model ecosystem*

Insecticides	Fish	Snail
Bux[R]	--	--
Sevin[R]	--	--
carbofuran	--	--
dieldrin	--	--
Orthene[R]	--	--
parathion	335	--
lindane and Aroclor 5460[R]	2,110	452
Herbicides		
alachlor	--	--
propachlor	--	--
Bladex[R]	--	--
Bentazon[R]	--	--
dicamba	--	--
2,4-D	--	--
pyrazon	--	--
Trifluralin[R] (sorghum treatment)	930	17,700
Trifluralin[R] (sand treatment)	4,200	153,000
Others		
2,5,2'-trichlorobiphenyl	6,400	5,795
2,5,2',5'-tetrachlorobiphenyl	11,863	39,439
2,4,5,2',5'-pentachlorobiphenyl	12,153	59,629
di-n-octyl phthalate	9,400	13,600
hexachlorophene	278	970
captan	--	--
Banomite[R]	--	--

*Accumulation factor equal concentration of chemical (ppm) in the organism/concentration of chemical (ppm) in the water

SECTION VI

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SECTION VIII

CHEMICAL NOMENCLATURE FOR COMPOUNDS EXAMINED IN A MODEL ECOSYSTEM

Compound	Name
Bux®	3:1 mixture of m-(1-ethylpropyl)phenyl N-methylcarbamate and m-(1-methylbutyl)phenyl N-methylcarbamate
Sevin®	1-napthyl N-methylcarbamate
carbofuran	2,2-dimethyl-2,3-dihydrobenzofuranyl 7-N-methylcarbamate
dieldrin	1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8a-octahydro-1,4-endo-exo-5,8-di-methanonapthalene
lindane	gamma isomer 1,2,3,4,5,6-hexachlorocyclohexane
Orthene®	O,S-dimethyl N-acetylphosphoramidothioate
parathion	O,O-diethyl-O-p-nitrophenyl phosphorothioate
alachlor	2-chloro-2',6'-diethyl-N-(methoxymethyl)-acetanilide
propachlor	2-chloro-N-isopropylacetanilide
Bladex®	2(4-chloro-6-ethylamino-s-triazin-2-ylamino 2-methylproprionitrile
Bentazon®	3-isopropyl-1-H-2,1,3-benzothiadiazin-4-(3H)-one-2,2-dioxide
dicamba	3,6-dichloro-2-methoxybenzoic acid
2,4-D	2,4-dichlorophenoxyacetic acid
Pyrazon®	5-amino-4-chloro-2-phenyl-3-(2H)-pyridazinone
Trifluralin®	α,α,α-trifluoro-2,6-dinitro-N,N-dipropyl-p-toluidine
Banomite®	benzoyl chloride-2,4,6-trichlorophenyl hydrazone
trichlorobiphenyl	2,5,2'-trichlorobiphenyl
tetrachlorobiphenyl	2,5,2',5'-tetrachlorobiphenyl
pentachlorobiphenyl	2,4,5,2',5'-pentachlorobiphenyl

Compound	Name
DOP	di-n-octyl phthalate
captan	N-trichloromethylthio-4-cyclohexene-1,2-dicarboximide
hexachlorophene	2,2-methylene-bis (3,4,6-trichlorophenol)